Dating of Young Groundwater

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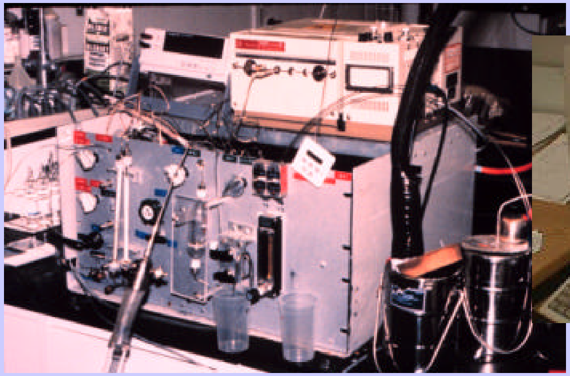
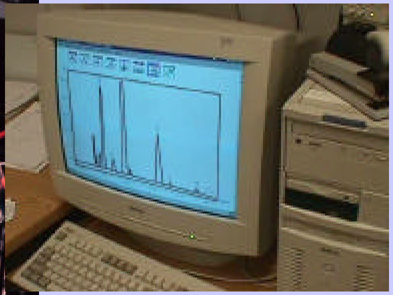
"Owing to dispersion, the "age" of a groundwater sample corresponds generally to a time distribution of many elementary flows. Thus, except in the theoretical case of a pure piston flow system, or of stationary waters entrapped in a geological formation, the concept of groundwater age has little significance"

J.-Ch. Fontes (1983) *in* Guidebook on Nuclear Techniques in Hydrology, IAEA

Approach to "Dating" Young GW

- **Collect water samples without contacting air.**
- **Minimize mixing effects by sampling monitoring wells with narrow screens.**
- **Analyze with high precision for CFCs, SF_6, ^3H, $^3H/^3He$, and others (multi-tracer approach).**
- **Age interpretation.** **Evaluate multiple tracer data in context of models of groundwater flow.**
- **Age is model dependent.**



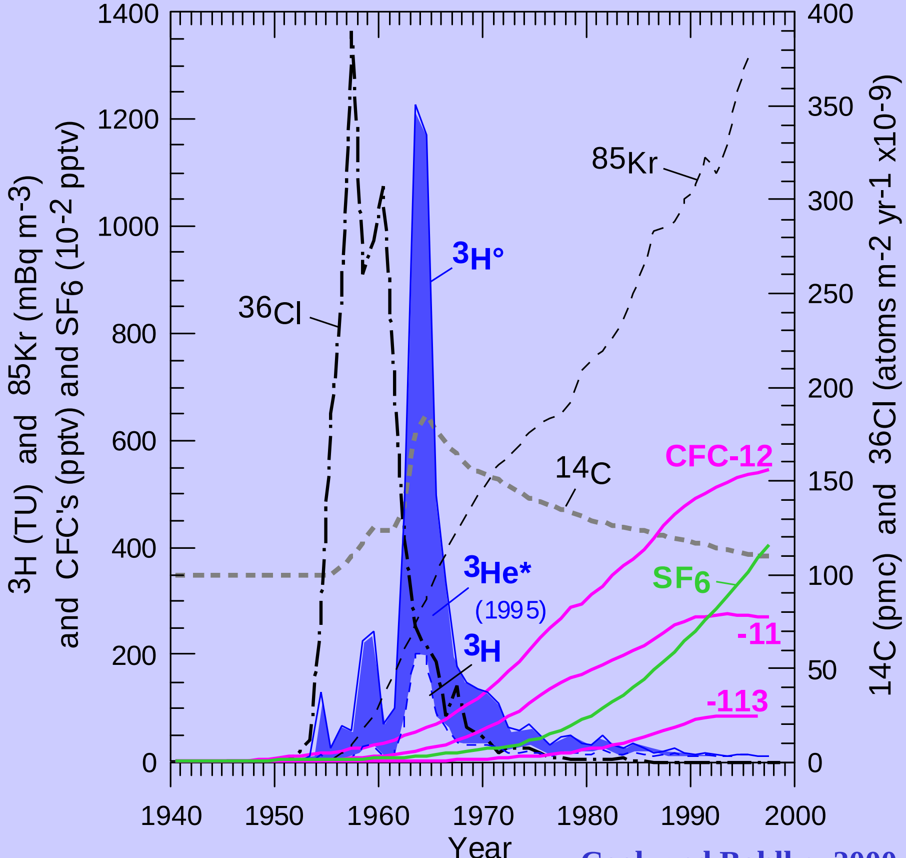


Age Interpretation

- **Comparison of simulated and observed tracer concentrations. Lumped-parameter models. Helps to have multiple tracers from the source, or a time series from the source, or multiple tracers from multiple sources in the system.**
- **Tracer plots. Method of comparing simulated and observed multiple tracer data; recognizing cases of possible piston flow and binary mixing (dilution); elimination of some mixing models.**
- **Flow-model calibration and simulation of age.**
- **All "ages", regardless of method, are model dependent.**

Selected Environmental Tracers
0-50 Year Timescale

tracer1b.grf (JK Böhlke) 4/22/03



Cook and Bohlke, 2000

- ^{3}H , $^{3}H/^{3}He$
- ^{85}Kr
- CFC-11, CFC-12, CFC-113
- SF_6
- Event Markers: ^{3}H, ^{36}Cl, ^{14}C
- Age: time elapsed since recharge

USGS

Tritium/Helium-3

- Half-life 12.3 years; decays to ^{3}He.
- Atmospheric thermonuclear weapons testing from the 1950’s, and especially in the period 1962-1963
- Initial ^{3}H measured
- Terrigenic He sources
- Dispersion around bomb peak
- Confinement of ^{3}He

USGS

Dating with $^{3}H/^{3}He$

Measured

$$^{3}H_{\boldsymbol{m}}$$

$$^{4}He_{m} = {}^{4}He_{eq} + {}^{4}He_{atm} + {}^{4}He_{ter}$$

$$Ne_{m} = Ne_{eq} + Ne_{atm}$$

$$d\,^{3}He = \left(\frac{R}{R_{a}} - 1 \right) \cdot 100$$

$$^{3}He_{m} = {}^{3}He_{eq} + {}^{3}He_{atm} + {}^{3}He_{ter} + {}^{3}He_{tri}$$

Some Definitions

N_{atm} = $(He/Ne)_{atm}$ = 0.288 for air excess
R_{atm} = $(^3He/^4He)_{atm}$ = 1.384×10^{-6} for air excess (R_a)
R_{ter} = $(^3He/^4He)_{ter}$ = 2×10^{-8} for radiogenic helium (R_{rad})
= 1×10^{-5} for mantle helium (R_{man})

$$Ne_m = Ne_{eq} + Ne_{atm}$$

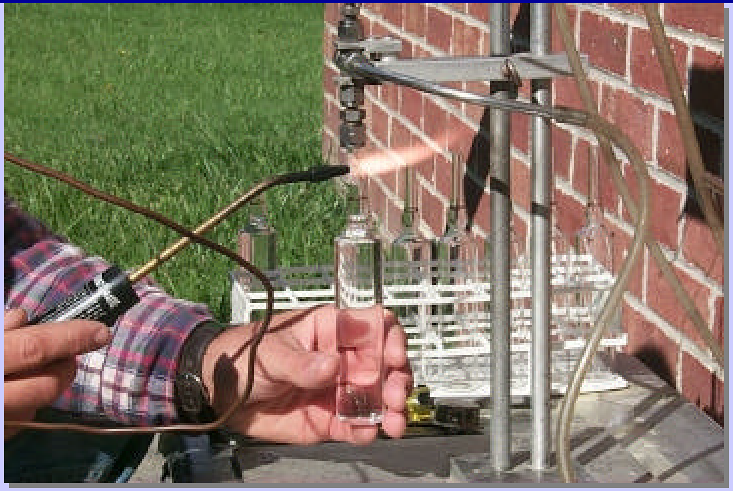
$$^4He_m = {}^4He_{eq} + N_{atm} \cdot Ne_{atm} + {}^4He_{ter}$$

$$^3He_m = R_{eq} \cdot {}^4He_{eq} + R_{atm} \cdot N_{atm} \cdot Ne_{atm} + R_{ter} \cdot {}^4He_{ter} + {}^3He_{tri}$$

$$^3He_{tri} = {}^4He_m \cdot (R_m - R_{ter}) - {}^4He_{eq} \cdot \left(R_{eq} - R_{ter}\right) - N_{atm} \cdot \left(Ne_m - Ne_{eq}\right) \cdot (R_{atm} - R_{ter})$$

$$\boxed{t = \frac{1}{l} \cdot \ln\left(1 + \frac{^3He_{tri}}{^3H_m}\right)}$$

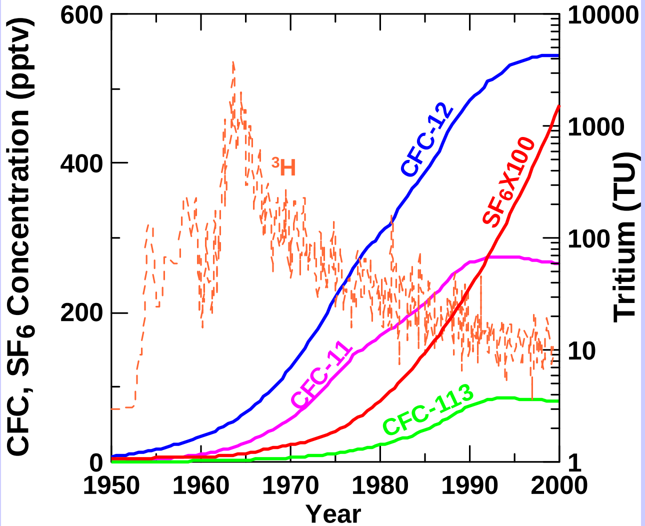
Chlorofluorocarbons

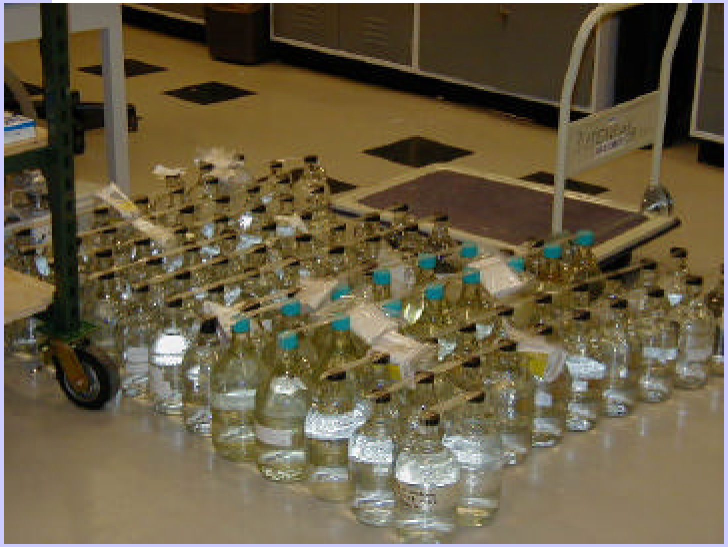


New bottle method of collection.
See http://water.usgs.gov/lab/cfc

- CFC-12 (CF_2Cl_2), 1930
- CFC-11 ($CFCl_3$), 1936
- CFC-113 ($C_2F_3Cl_3$), 1944
- Input smooth, increasing until 1990s (dating range ~1950 to early 1990s).
- Stable in aerobic environments.
- In future- dual ages.
- Use of ratios.
- Can detect post 1940’s water.
- Collection/analysis not overly labor intensive.
- Problems with contamination, degradation (anoxic), sorption?

Sulfur Hexafluoride

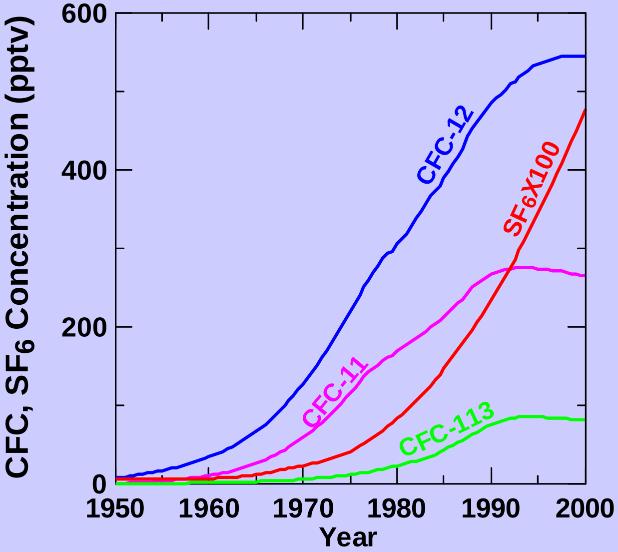




- Electrical insulator in high voltage switches
- First produced 1953
- Very low solubility in water.
- Does not degrade
- Terrigenic source
- Dating range: 1970-modern.
- Smooth input, increasing in air at 6%/yr; 5 pptv today.

Dating with CFCs and SF_6

- **Henry's law solubility** $C_i = K_H \, x \, p_i$
- **Requirements:**

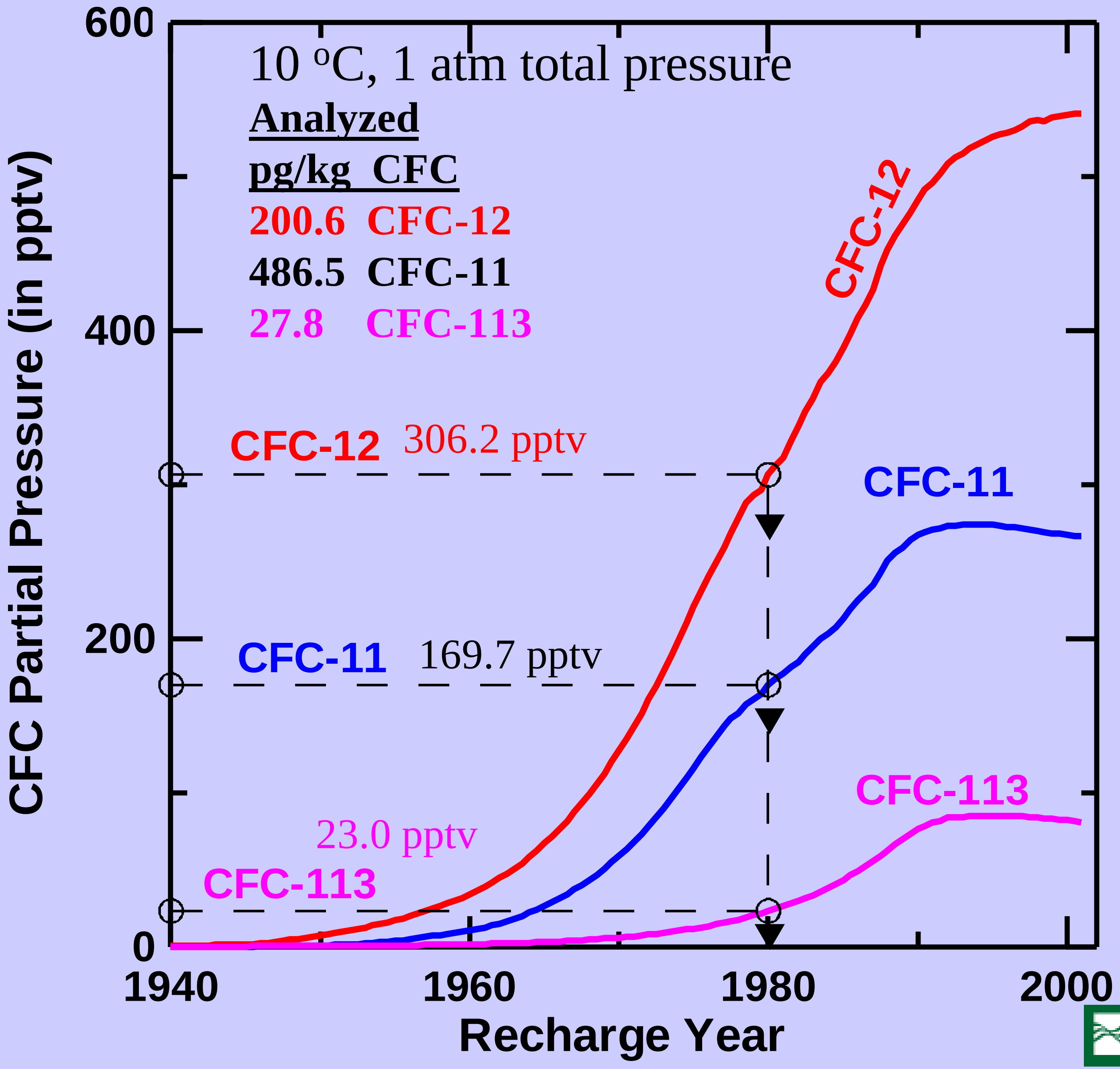


➢ Gas-water equilibrium at recharge

➢ Recharge temperature

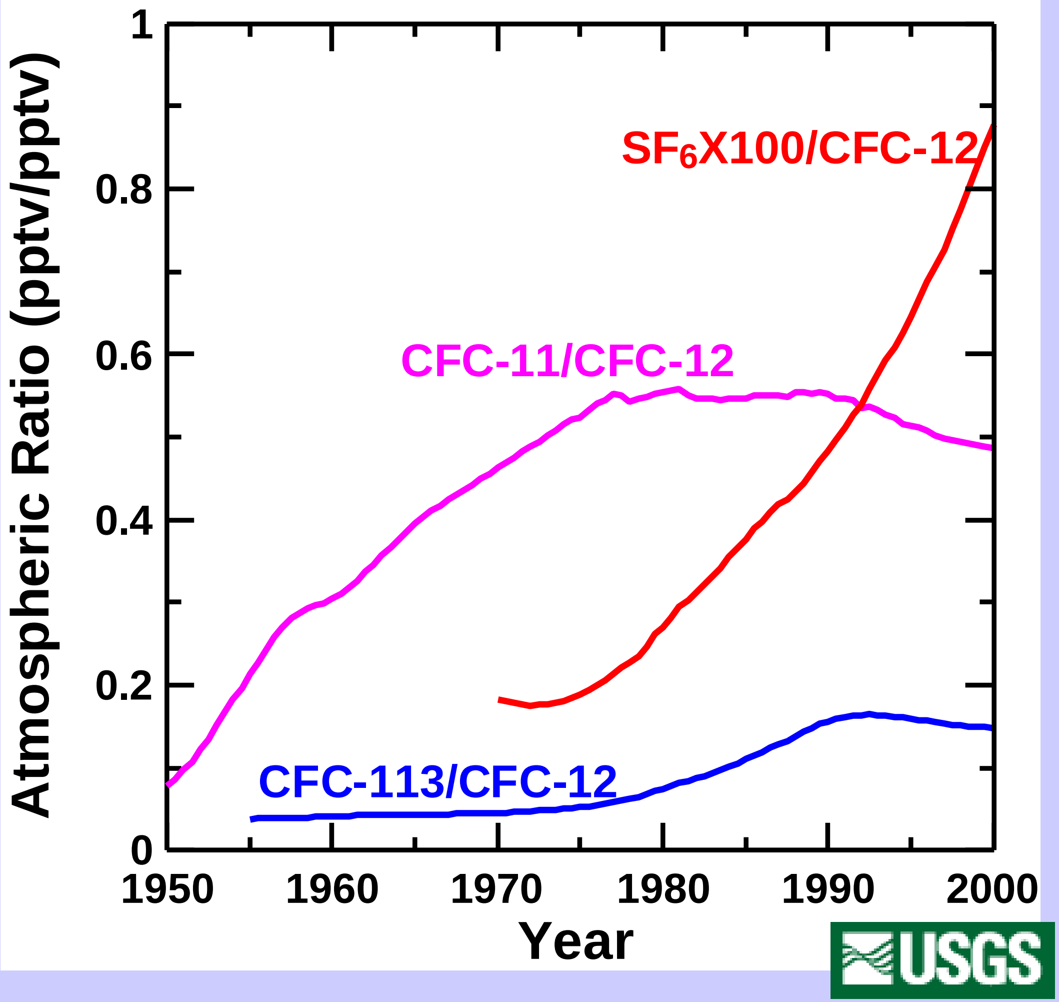
➢ Barometric pressure at recharge

➢ Knowledge of atmospheric history of the gas

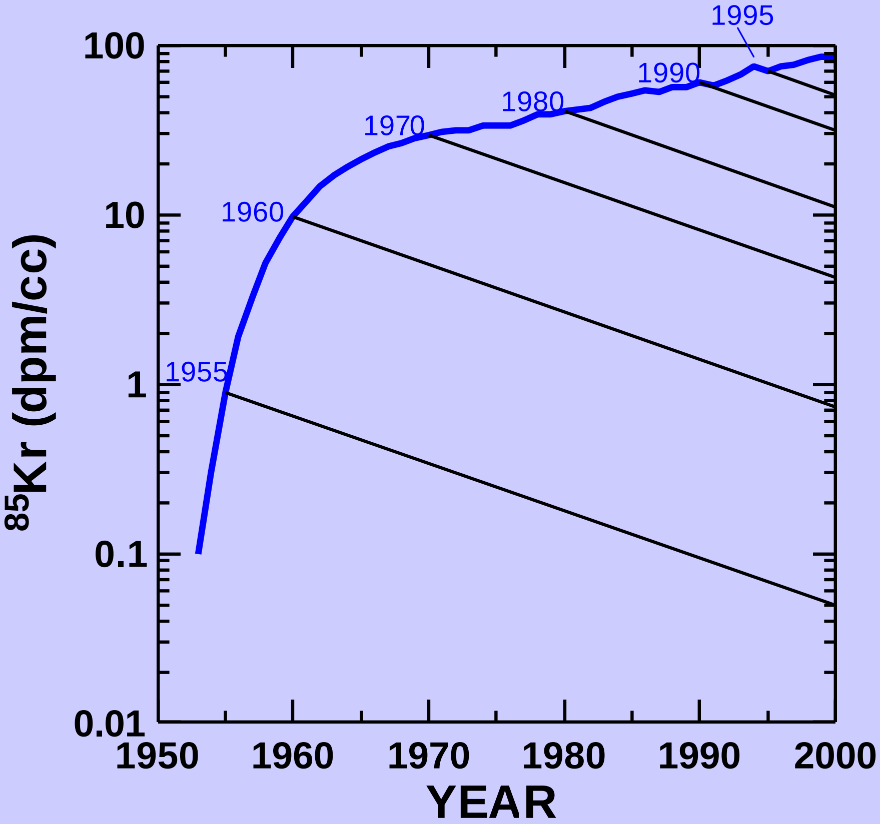

10 °C, 1 atm total pressure
Analyzed
pg/kg CFC
200.6 CFC-12
486.5 CFC-11
27.8 CFC-113
CFC-12 306.2 pptv
CFC-11 169.7 pptv
23.0 pptv
CFC-113
CFC-12
CFC-11
CFC-113
600
400
200
0
1940
1960
1980
2000
CFC Partial Pressure (in pptv)
Recharge Year

Dating with Ratios

In binary mixtures of young and old (pre-tracer), the tracer ratio in the young fraction is preserved.



Krypton-85



- Radioactive noble gas with a half-life of 10.76 years.
- ^{85}Kr in the atmosphere has steadily increased since the mid-1950s.
- Interpreted age insensitive to recharge temperature, altitude, etc.
- Does not degrade.
- Atmosphere is only significant source.
- Although difficult to collect and analyze, even a few ^{85}Kr can often help resolve questions.

USGS

Limitations

$^{3}H/^{3}He$

- Cost
- Terrigenic He
- Bubbles, Gas-stripping, confinement
- Mixing

SF_6

•Terrigenic SF_6
•Mixing

CFCs

- Contamination
- Degradation
- Mixing

^{85}Kr

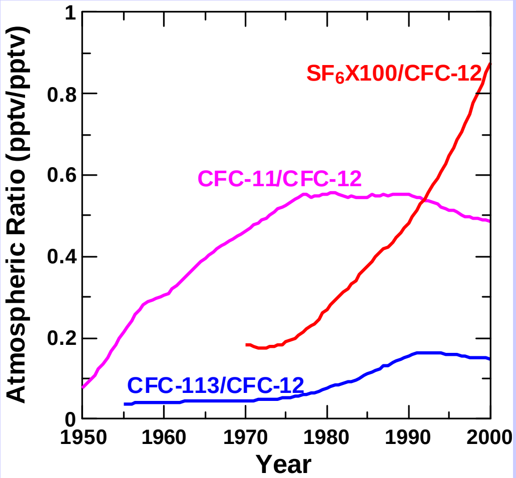
•Very difficult collection and analysis
•No labs available to us

Some Practical Applications
(of interpreted age information)

- Estimate recharge rates.
- Calibrate models of groundwater flow.
- Estimate rates of geochemical and microbiological processes **(natural remediation).**
- Evaluate susceptability to contamination.
- Retrieve historical records of contaminant loading to aquifers.
- Estimate remediation times.

USGS

Tracer Method of dating the young fraction in binary mixtures of young and old



- **CFC pptv ratio defines age of young fraction.**
- **% young water $(pptv_{(measured)} / pptv_{(ratio\ year)}) \times 100$**

- **Cannot date outside range for ratio.**
- **Cannot use if one of the CFCs in the selected ratio is "contaminated", even if ratio is "in range".**
- **Ratio-based age must be less than (younger than) apparent (piston flow) model ages for both CFCs in the ratio.**

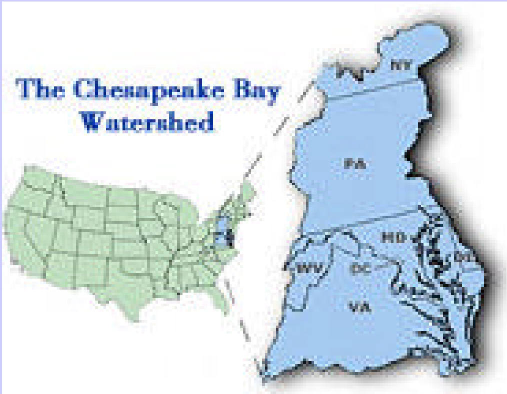
$^{3}H/^{3}He$ Age Applies to that of the Young Fraction in Simple Binary Mixtures

$^{3}H/^{3}He$ Age is based on an isotope ratio.

$$t = \frac{1}{l} \cdot \ln\left(1 + \frac{^{3}He_{tri}}{^{3}H_{m}}\right)$$

λ = decay constant = ln 2/$t_{1/2}$ = 0.05635 year^{-1}

$t_{1/2}$ = 12.3 years



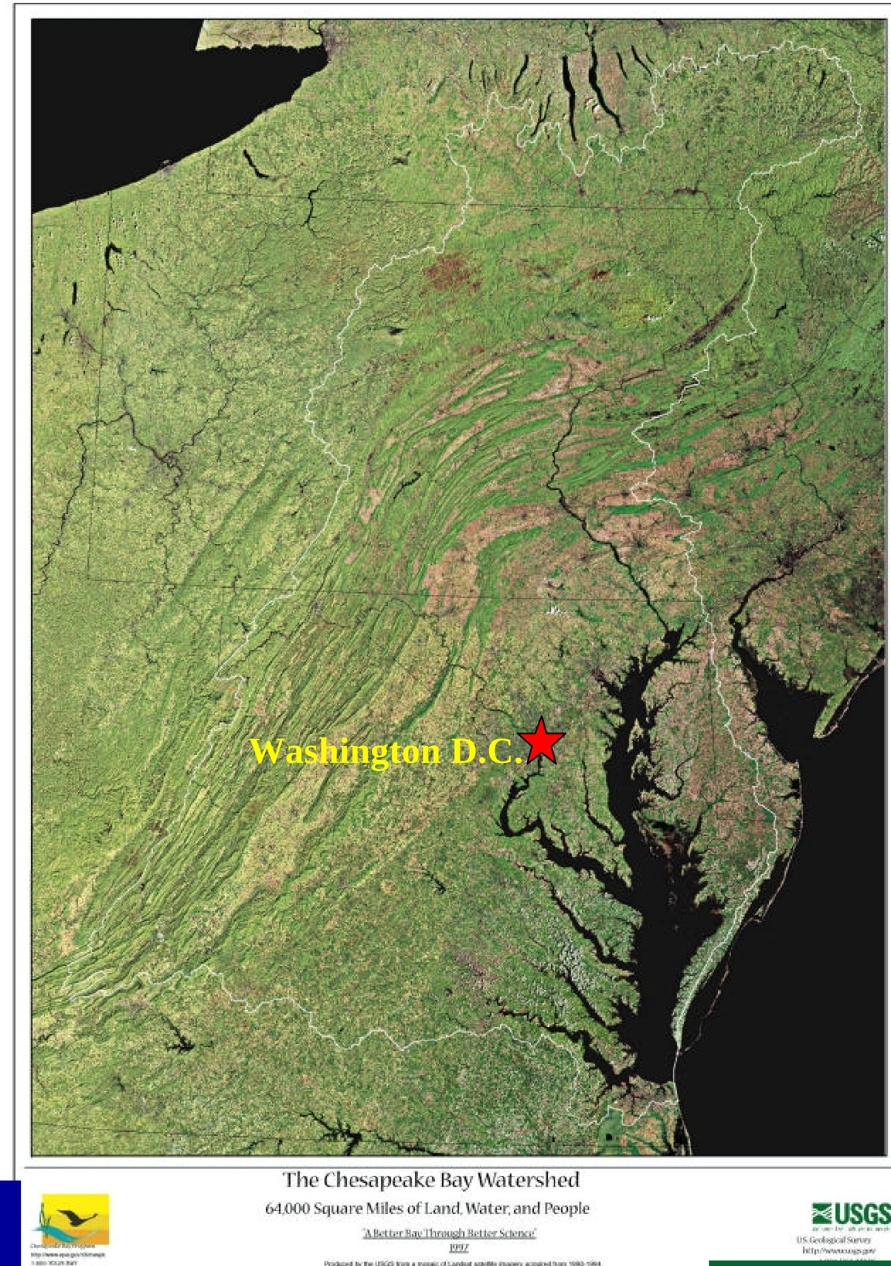
Chesapeake Bay Watershed

Region of 165,000 km^2 over parts of NY, PA, MD, DE, VA, and WV.

Evaluate residence times and nitrate transport in groundwater discharging to streams in the watershed.

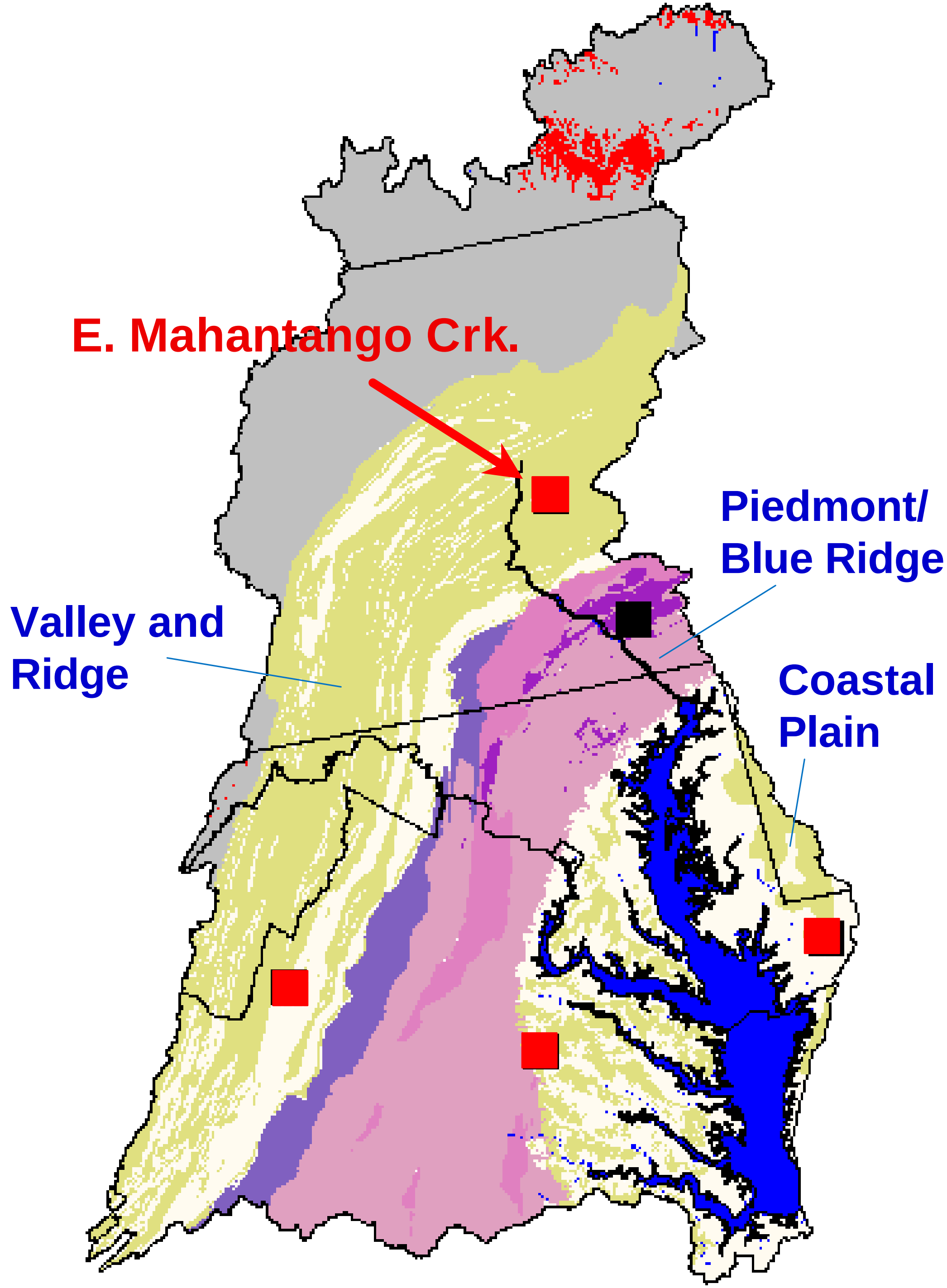
Assess lag time between changes at the land surface and the response in the base-flow component of groundwater discharge to the bay.

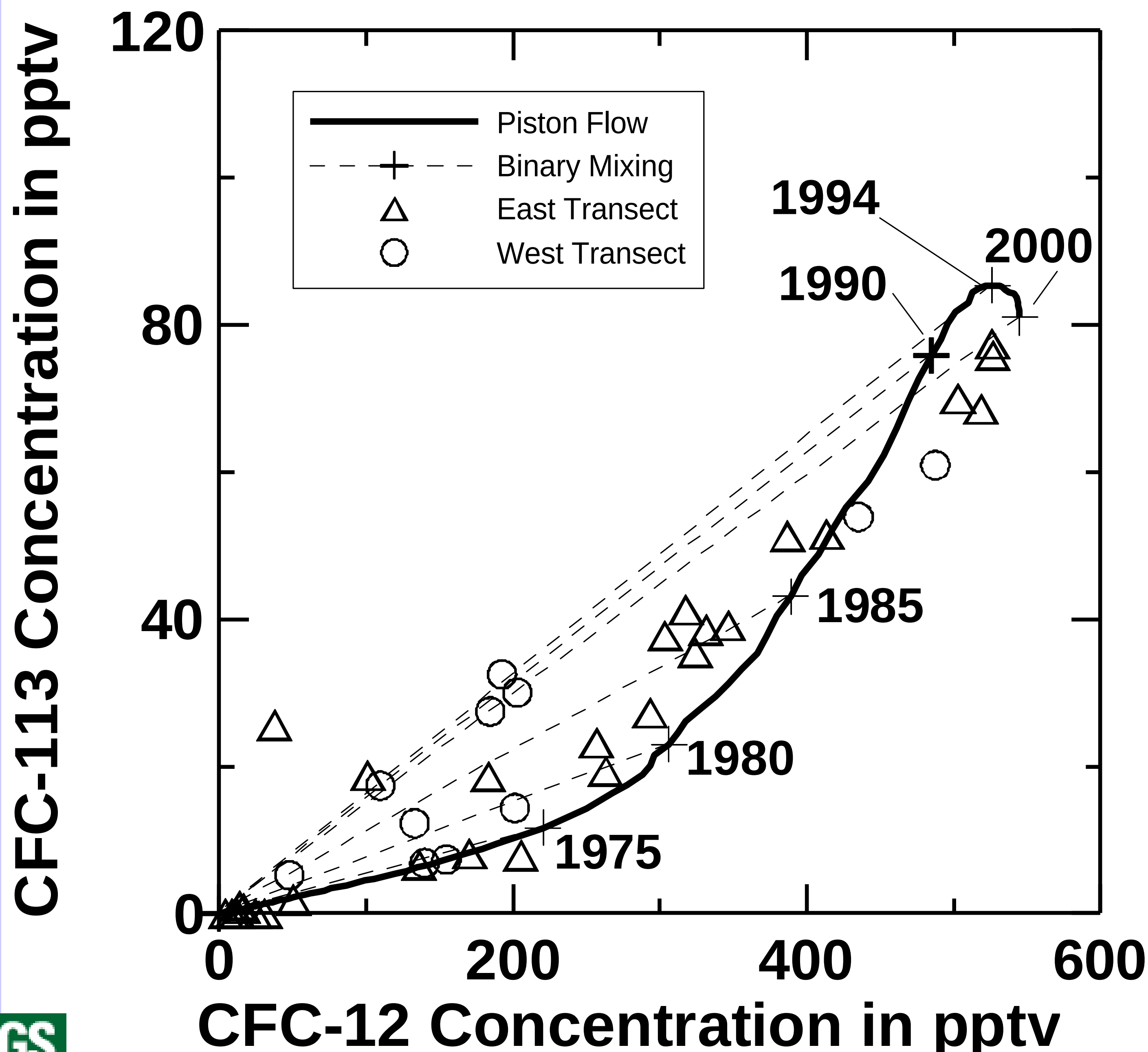
Lindsey and others, 2003, USGS WRIR 03-4035, http://pa.water.usgs.gov/reports/wrir03-4035.pdf



USGS Chesapeake Bay watershed nutrient study

- Model influx of nitrogen into Bay
- “Targeted watersheds” in high-nitrate-source areas underlain by varied geology, including fractured bedrock
- What is effect of bedrock geology on base flow and ground-water travel times?




CFC-113 Concentration in pptv
CFC-12 Concentration in pptv
0
40
80
120
0
200
400
600
Piston Flow
Binary Mixing
East Transect
West Transect
1994
2000
1990
1985
1980
1975

USGS

East Piezometer Transect

--Preferred CFC-12 ages NE of stream are older...

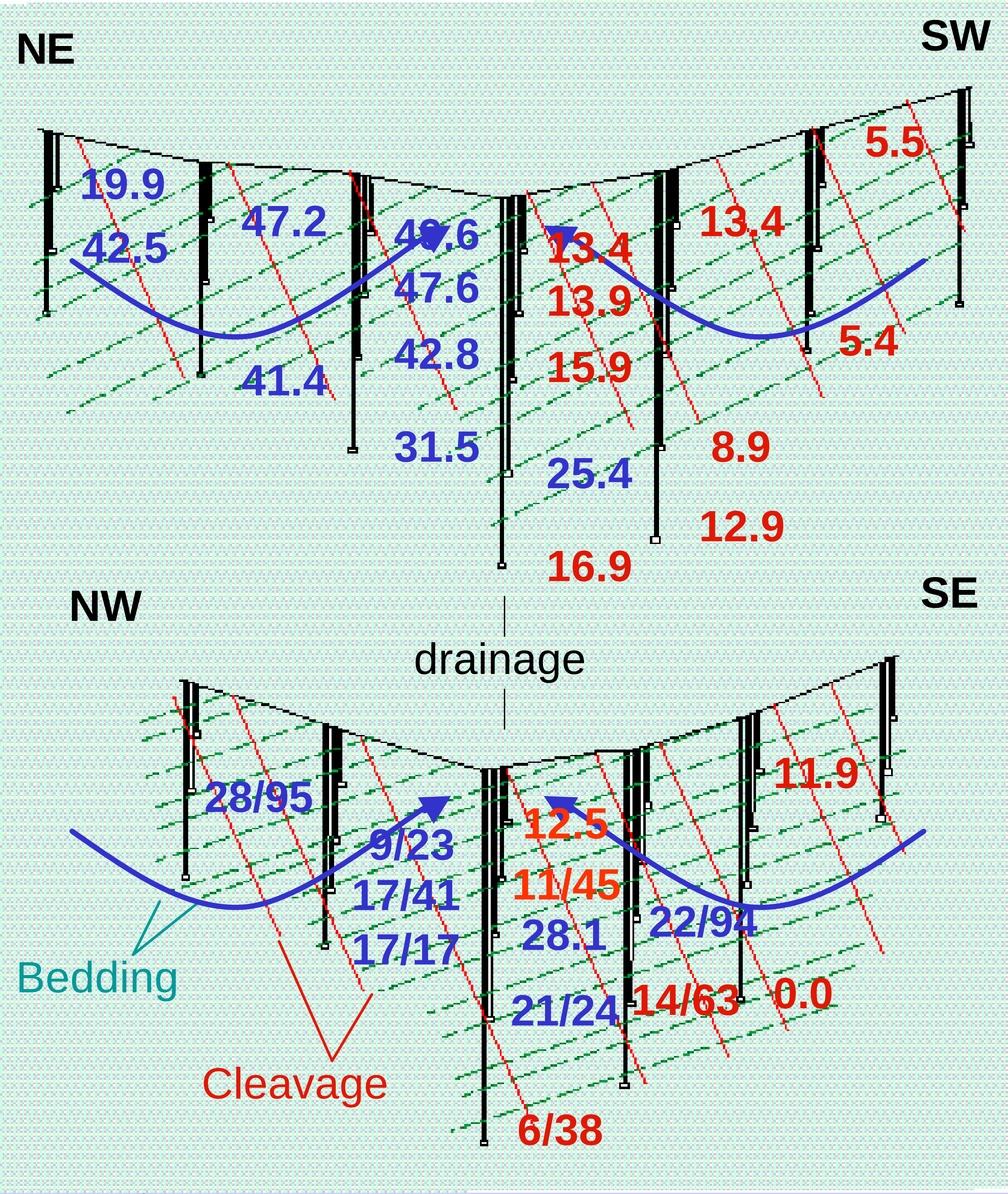
..than those underneath and SW of stream

..although these ages are really mixture ages!

West Piezometer Transect

--Ages are even more mixed, but % of young water (2nd #) shows older waters generally prevailing to NW

…and younger to SE



Burton et al. 2002

Geochemical Reactions

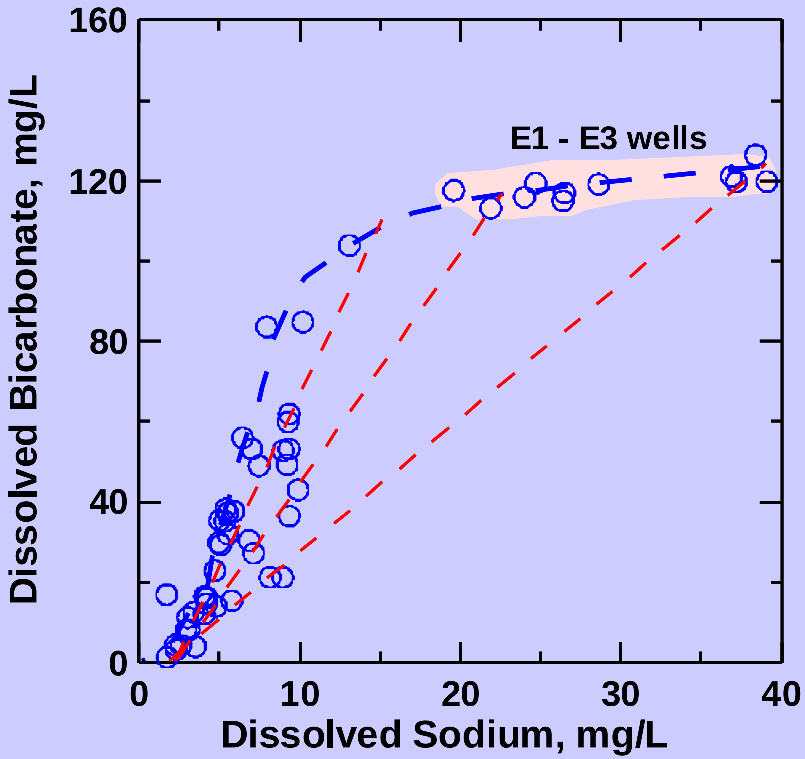
Calcite dissolution

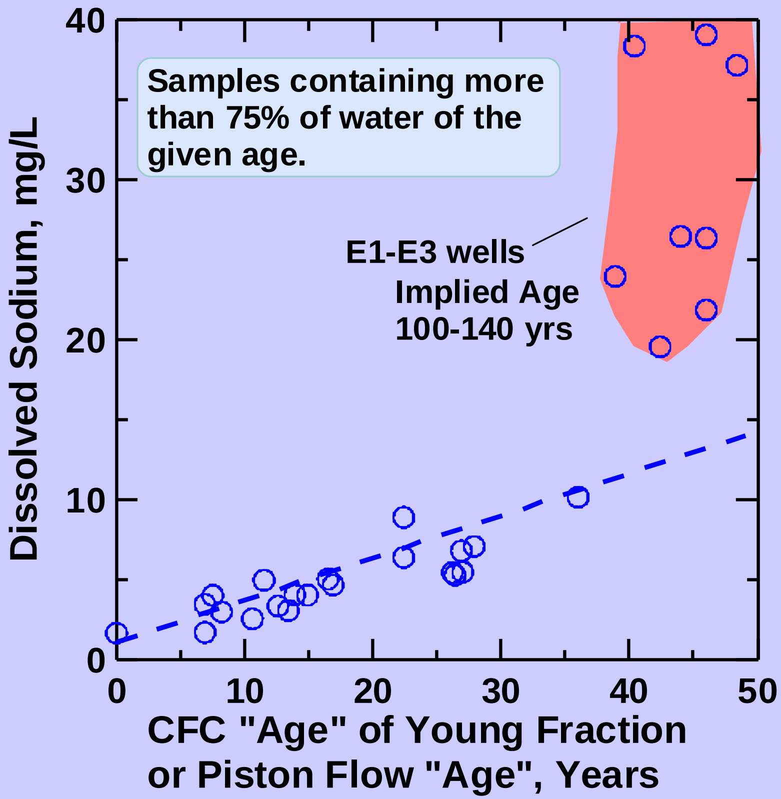
Ca/Na cation exchange

Plagioclase feldspar weathering

Evolve to Na-HCO_3 water

Calibration of Local Reaction Rate, and "Dating" Beyond the CFC Range





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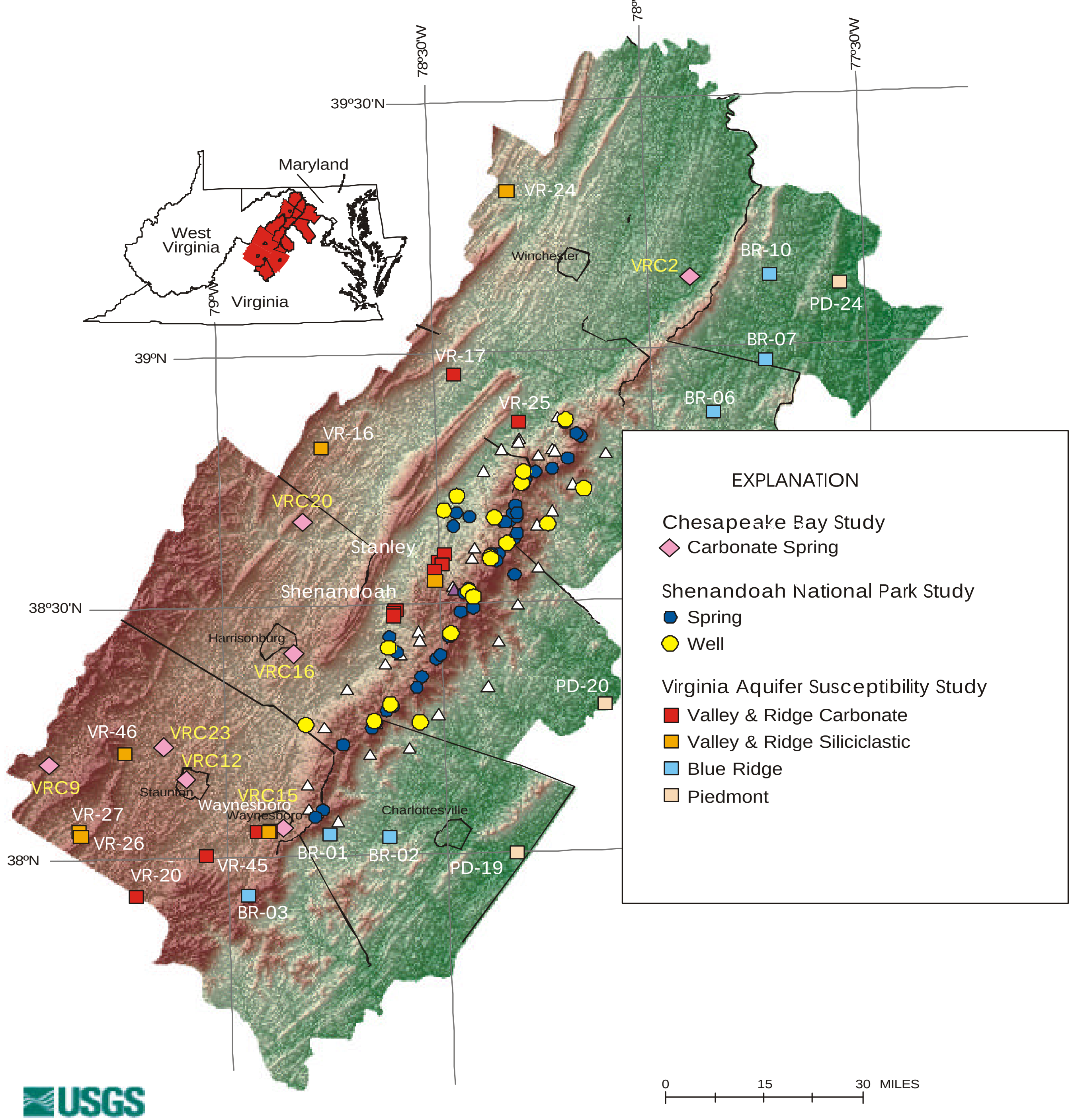


39°30'N
39°N
38°30'N
38°N
78°30'W
77°30'W
79°W
Maryland
West Virginia
Virginia
Winchester
Stanley
Shenandoah
Harrisonburg
Staunton
Waynesboro
Charlottesville
VR-24
VRC2
BR-10
PD-24
BR-07
VR-17
VR-25
BR-06
VR-16
VRC20
VRC16
PD-20
VR-46
VRC23
VRC12
VRC9
VRC15
VR-27
VR-26
VR-45
VR-20
BR-01
BR-02
BR-03
PD-19
EXPLANATION
Chesapeake Bay Study
Carbonate Spring
Shenandoah National Park Study
Spring
Well
Virginia Aquifer Susceptibility Study
Valley & Ridge Carbonate
Valley & Ridge Siliciclastic
Blue Ridge
Piedmont
0
15
30 MILES
USGS

Numbers of Samples from the Valley and Ridge Carbonates

Source	Chloro-fluoro-carbons	Tritium	Tritium/ Helium-3
Springs	69	25	18
Public Supply wells	11	11	9
Domestic wells	11	3	3
Monitoring wells	9	9	9
Total Samples	100	48	39

Although all samples are from Valley and Ridge carbonates, the extent of karst development is not well known.

Hydrogeology of Carbonate Terranes of the Valley & Ridge Province

Soil & Regolith

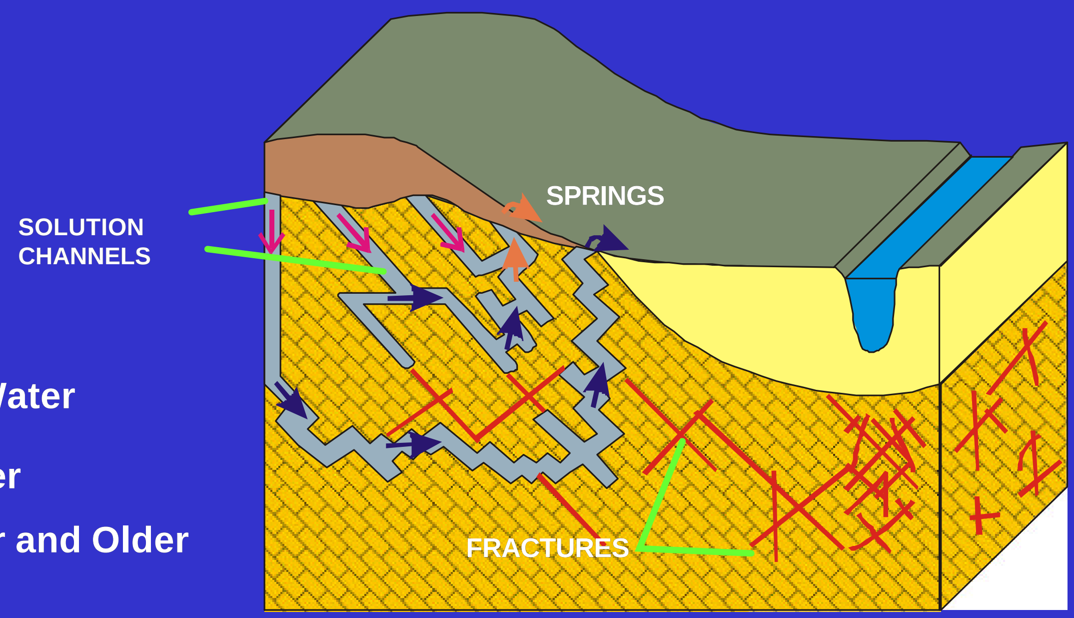
Alluvium

Limestone

Younger Ground Water

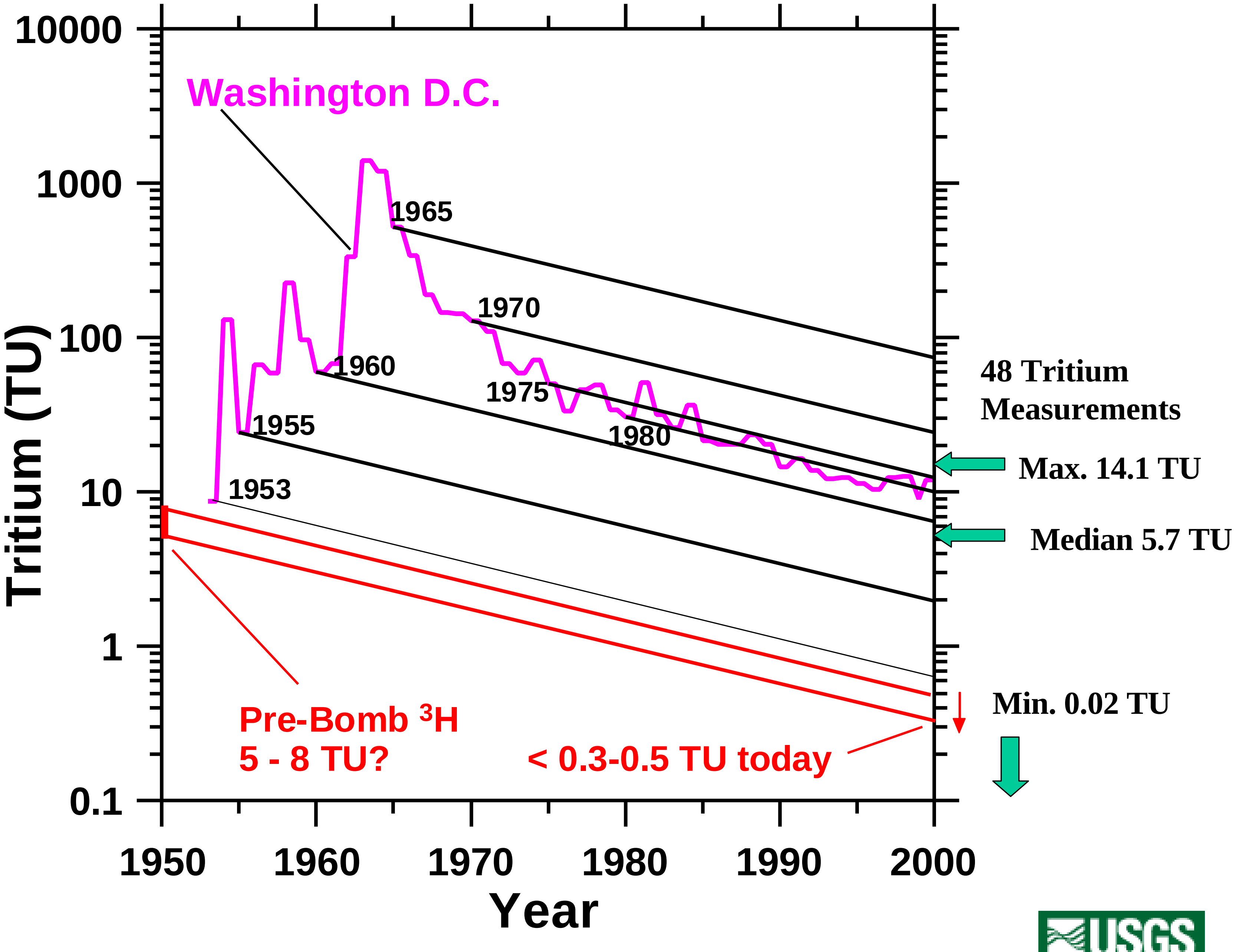
Older Ground Water

Mixture of Younger and Older Ground Water

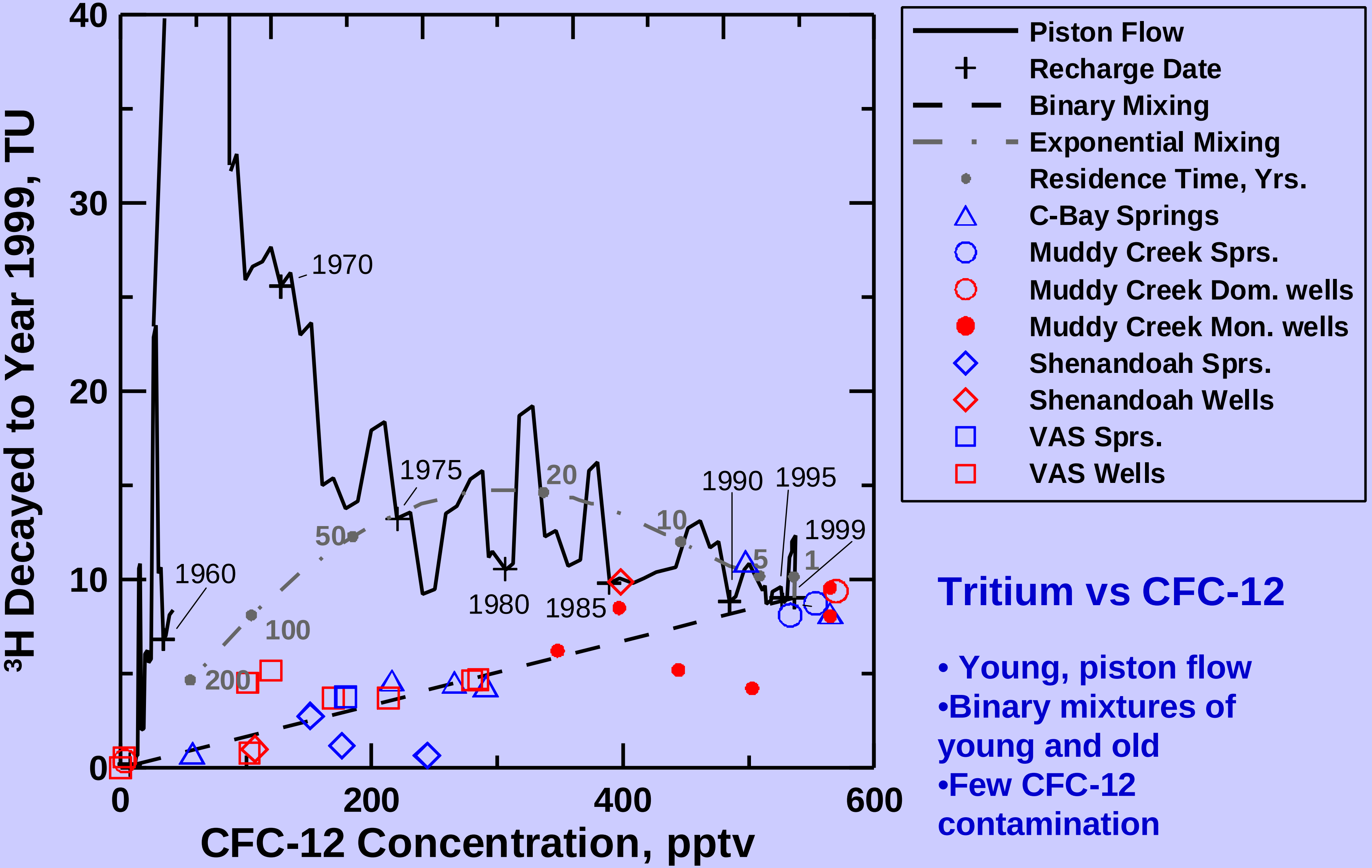


Modified from Brahana and others, 1986

NOT TO SCALE

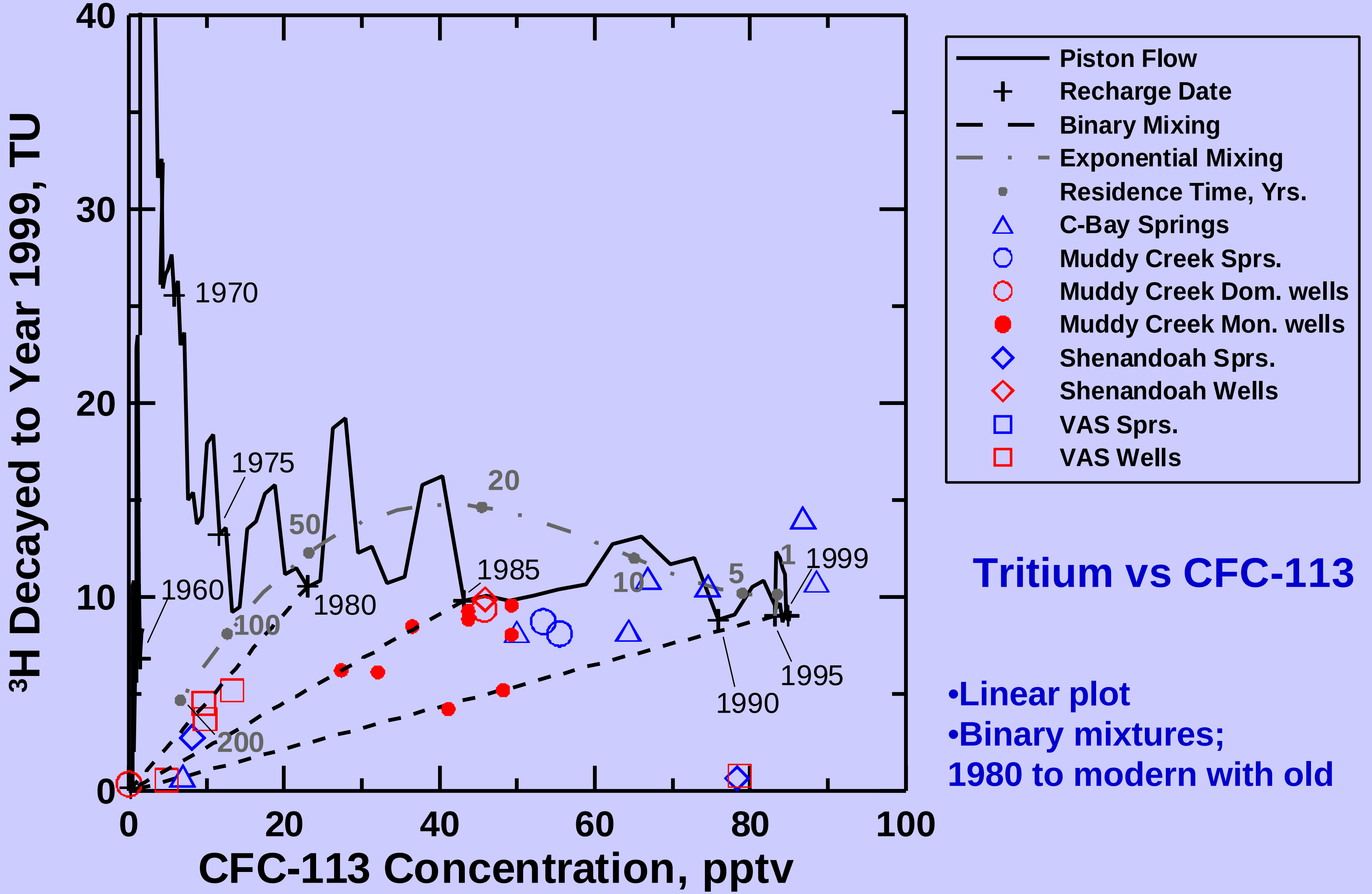


Washington D.C.
Tritium (TU)
10000
1000
100
10
1
0.1
1965
1970
1960
1975
1955
1980
1953
48 Tritium Measurements
Max. 14.1 TU
Median 5.7 TU
Min. 0.02 TU
Pre-Bomb ^{3}H
5 - 8 TU?
< 0.3-0.5 TU today
1950
1960
1970
1980
1990
2000
Year



Tritium vs CFC-12

- Young, piston flow
- Binary mixtures of young and old
- Few CFC-12 contamination



Tritium vs CFC-113

- Linear plot
- Binary mixtures; 1980 to modern with old

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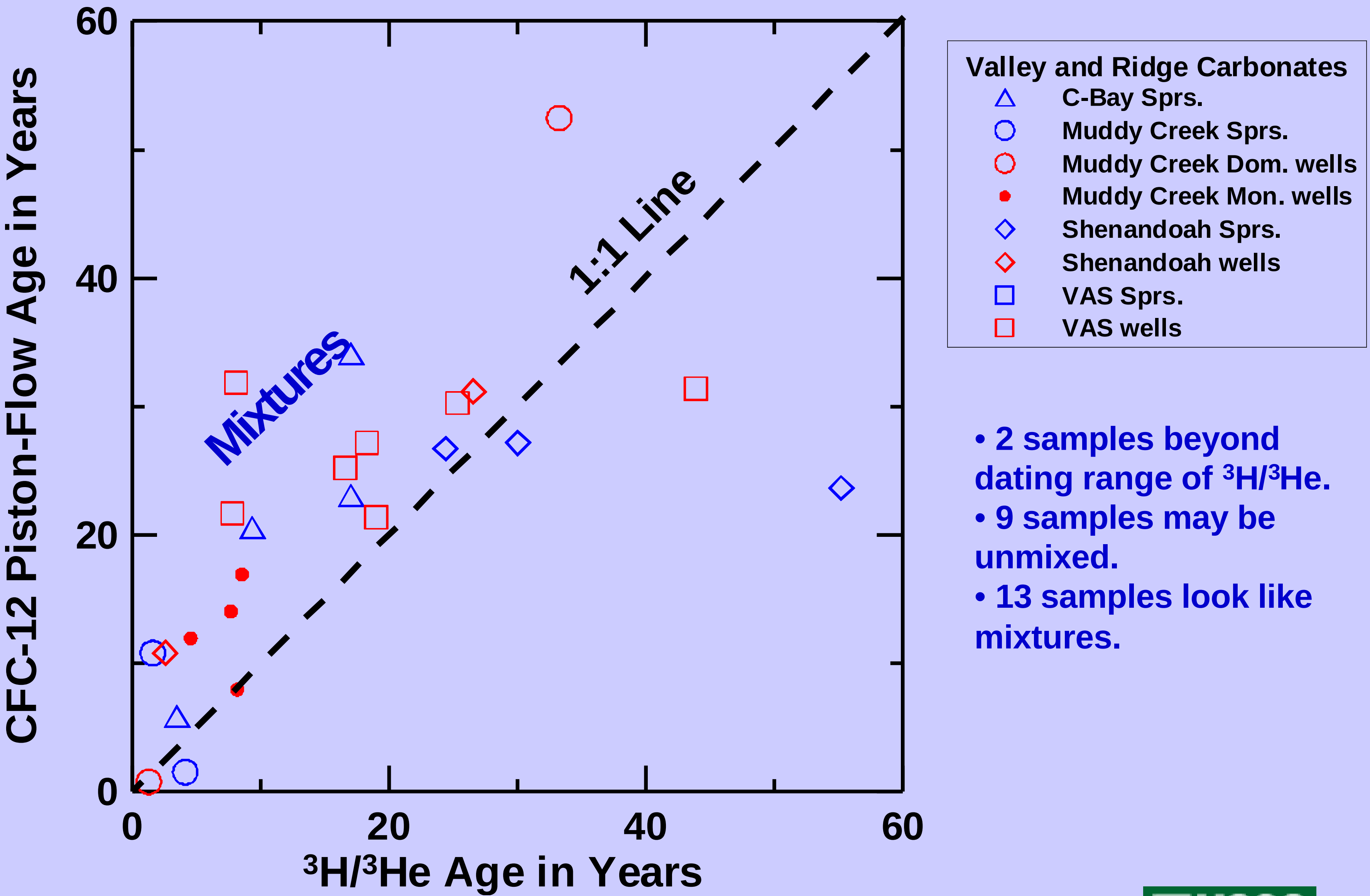
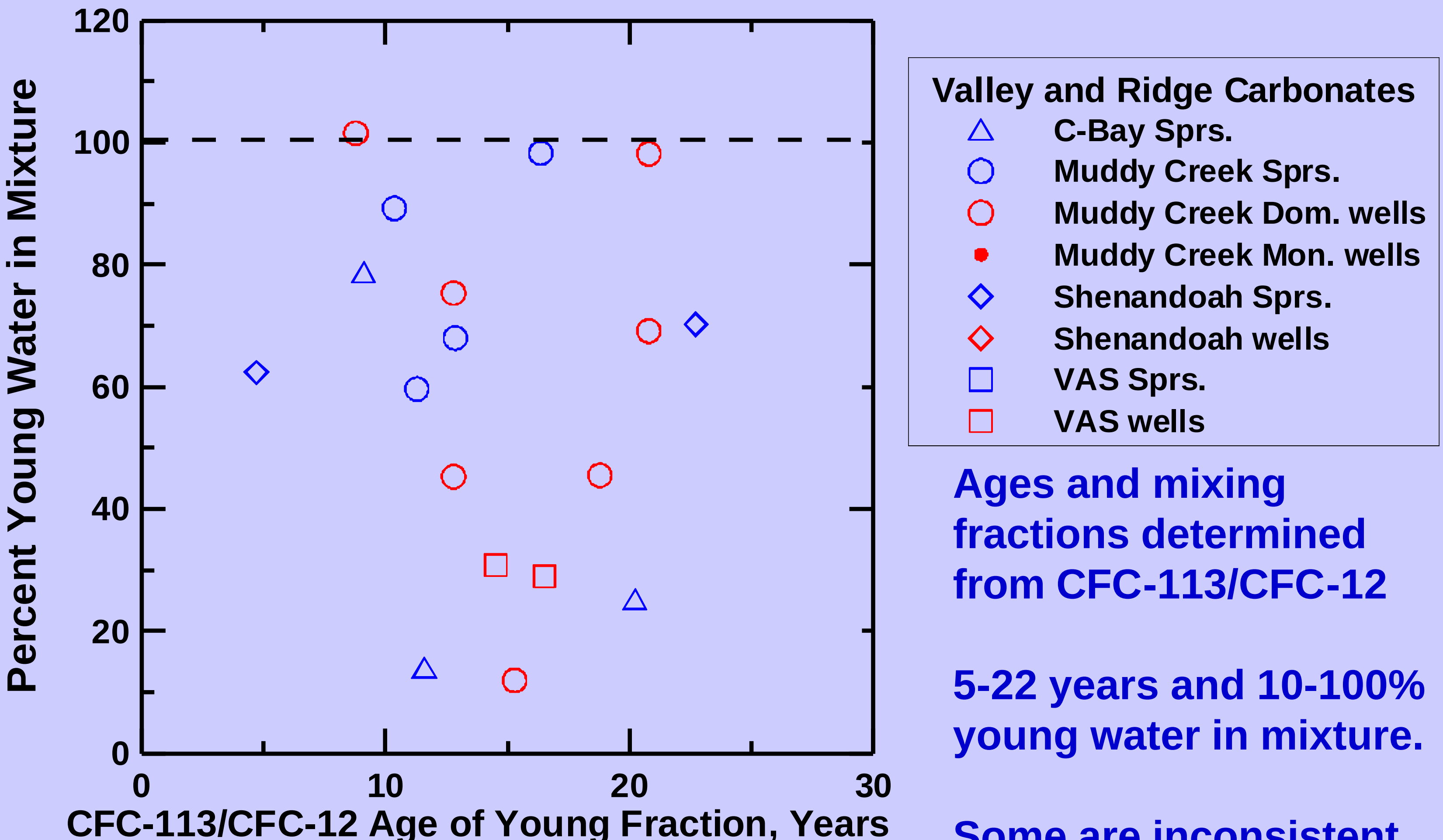


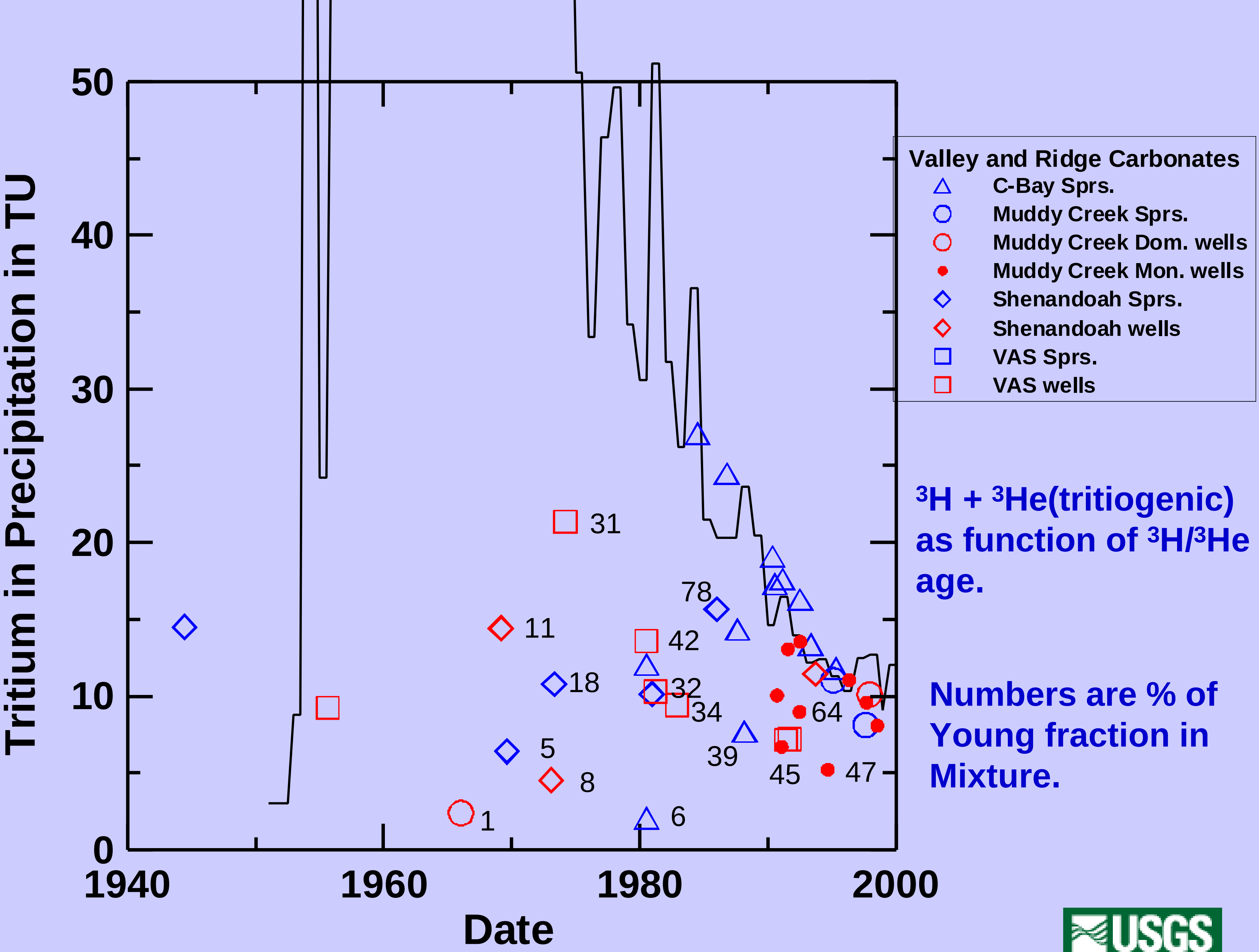
- 2 samples beyond dating range of $^3H/^3He$.
- 9 samples may be unmixed.
- 13 samples look like mixtures.



Ages and mixing fractions determined from CFC-113/CFC-12

5-22 years and 10-100% young water in mixture.

Some are inconsistent with ^{3}H (CFC contam.)



^3H + ^3He(tritiogenic) as function of $^3H/^3He$ age.

Numbers are % of Young fraction in Mixture.

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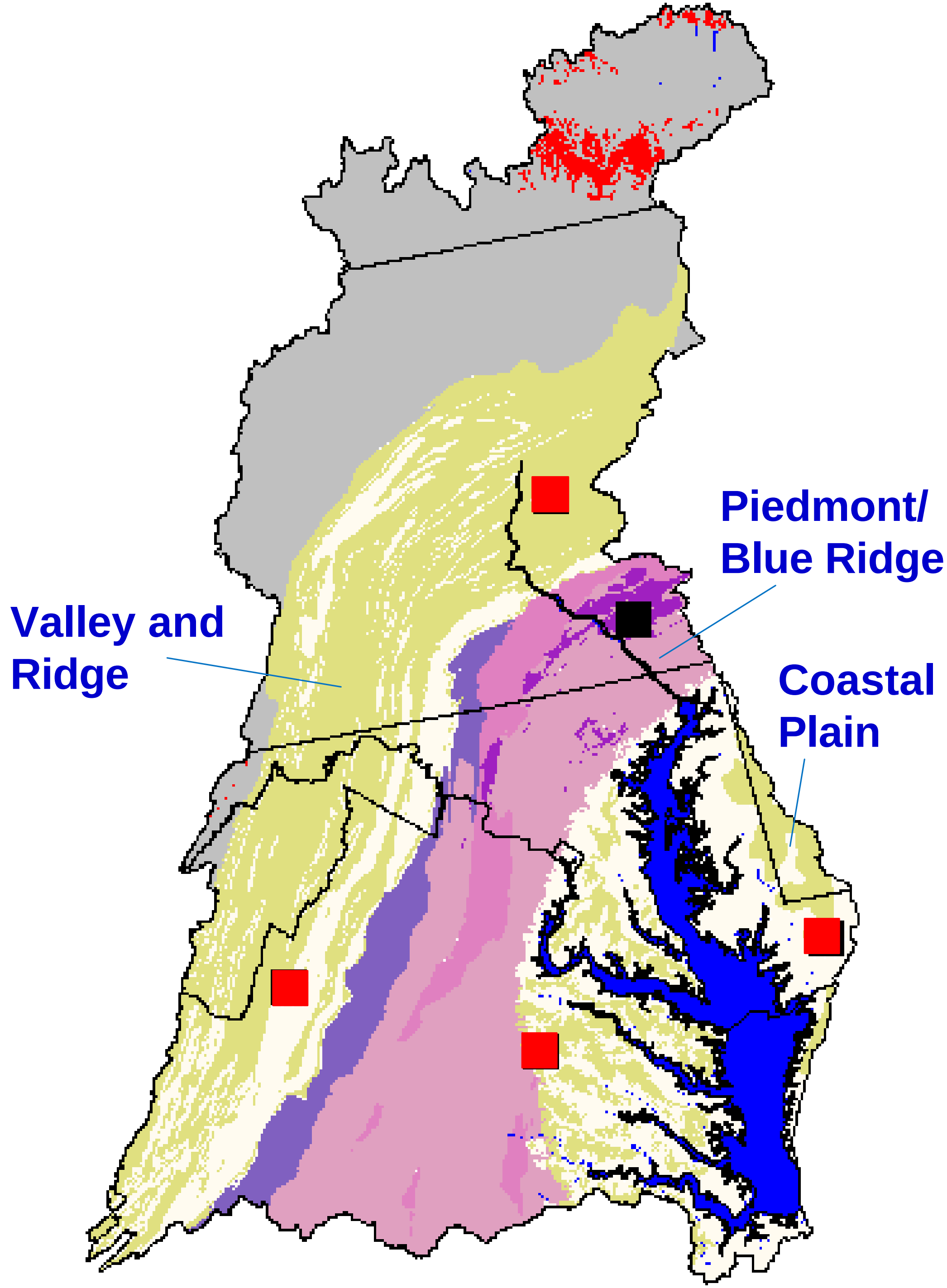
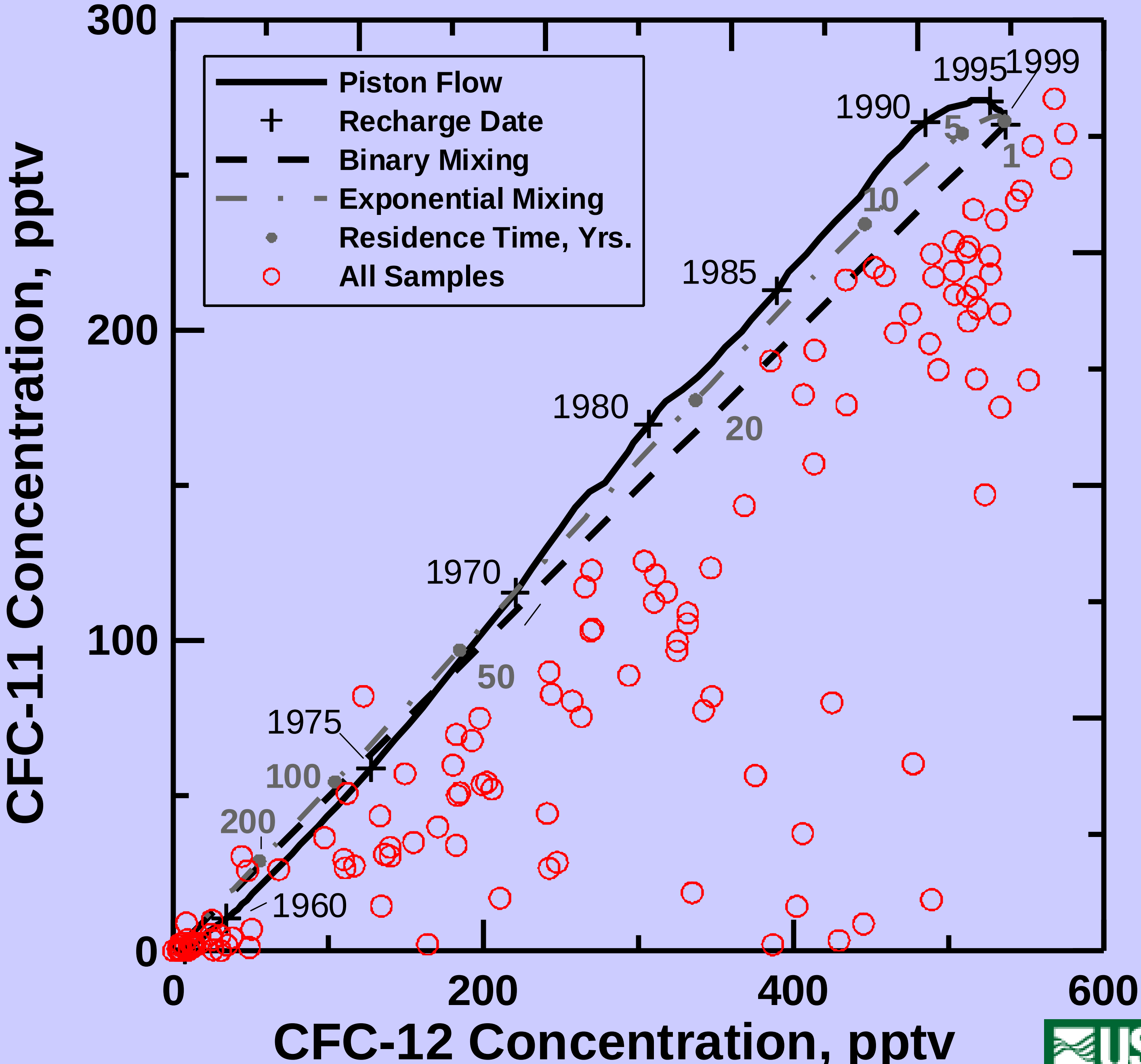
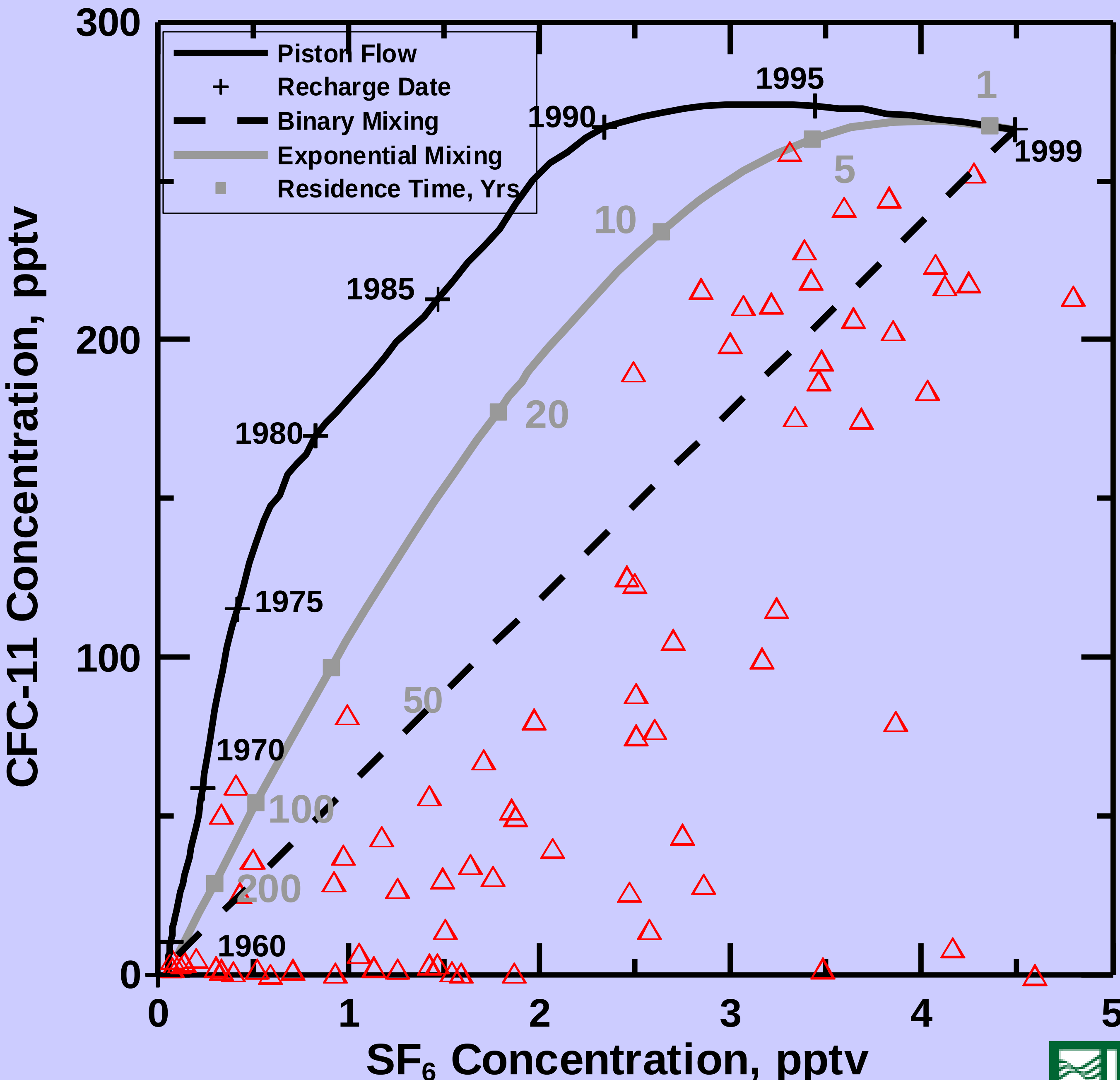
USGS Chesapeake Bay watershed nutrient study

- Relations among ^3H, CFCs, and SF_6

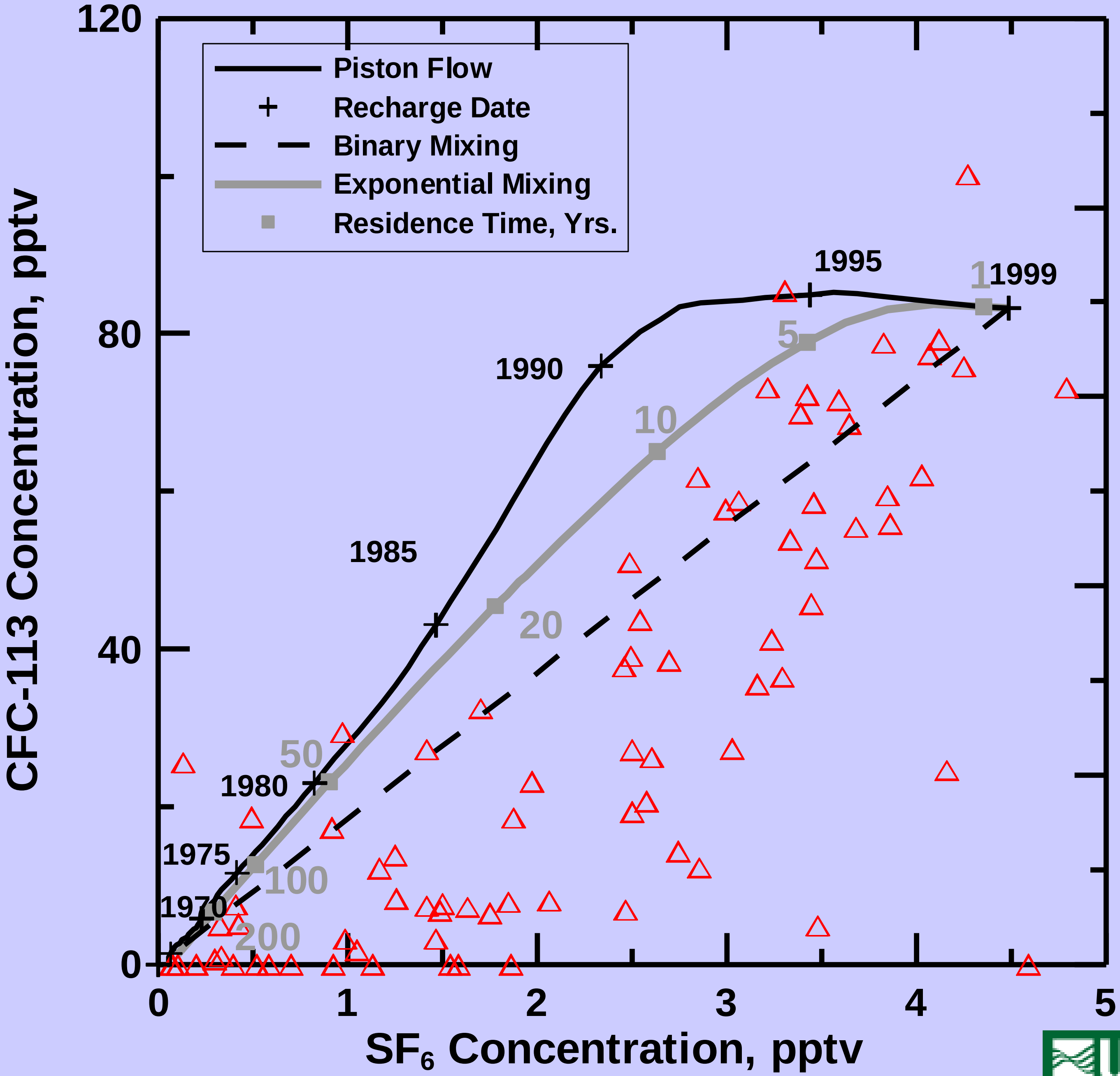




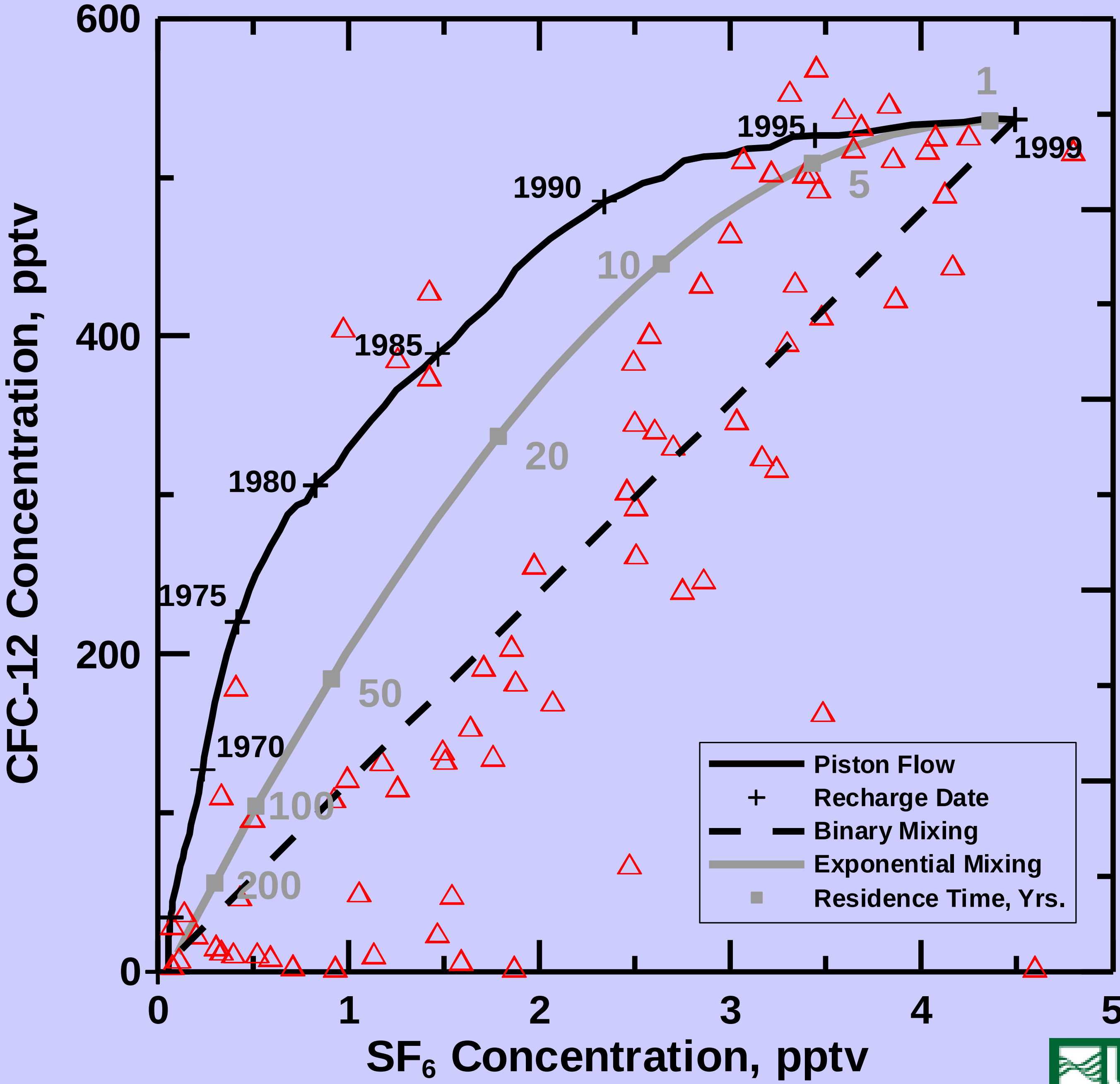
Piston Flow
Recharge Date
Binary Mixing
Exponential Mixing
Residence Time, Yrs.
All Samples
1960
1975
1970
1980
1985
1990
1995
1999
200
100
50
20
10
5
1
0
100
200
300
400
600
CFC-11 Concentration, pptv
CFC-12 Concentration, pptv



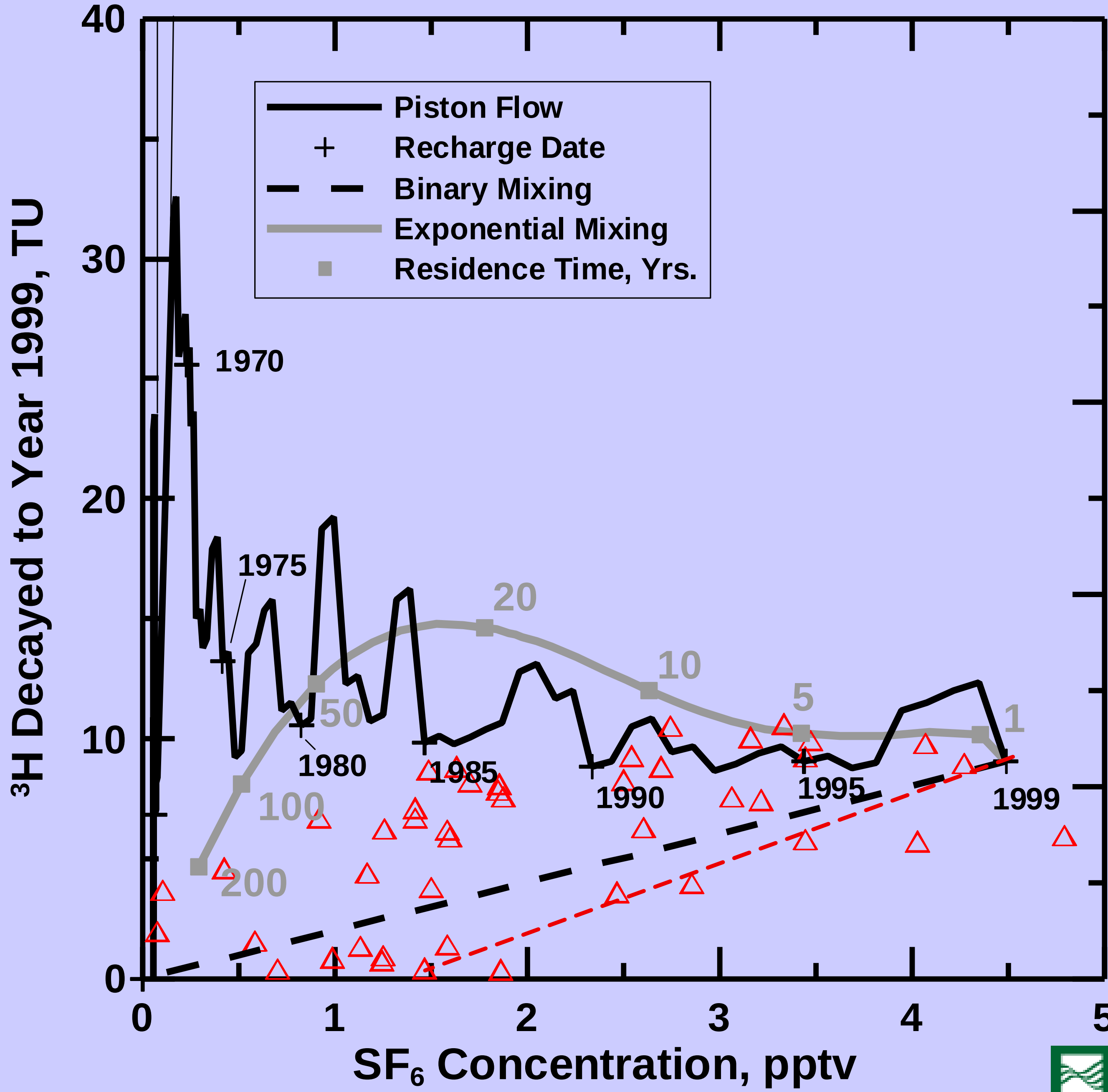
300
200
100
0
0
1
2
3
4
5
CFC-11 Concentration, pptv
SF6 Concentration, pptv
Piston Flow
Recharge Date
Binary Mixing
Exponential Mixing
Residence Time, Yrs
1960
1970
1975
1980
1985
1990
1995
1999
1
5
10
20
50
100
200



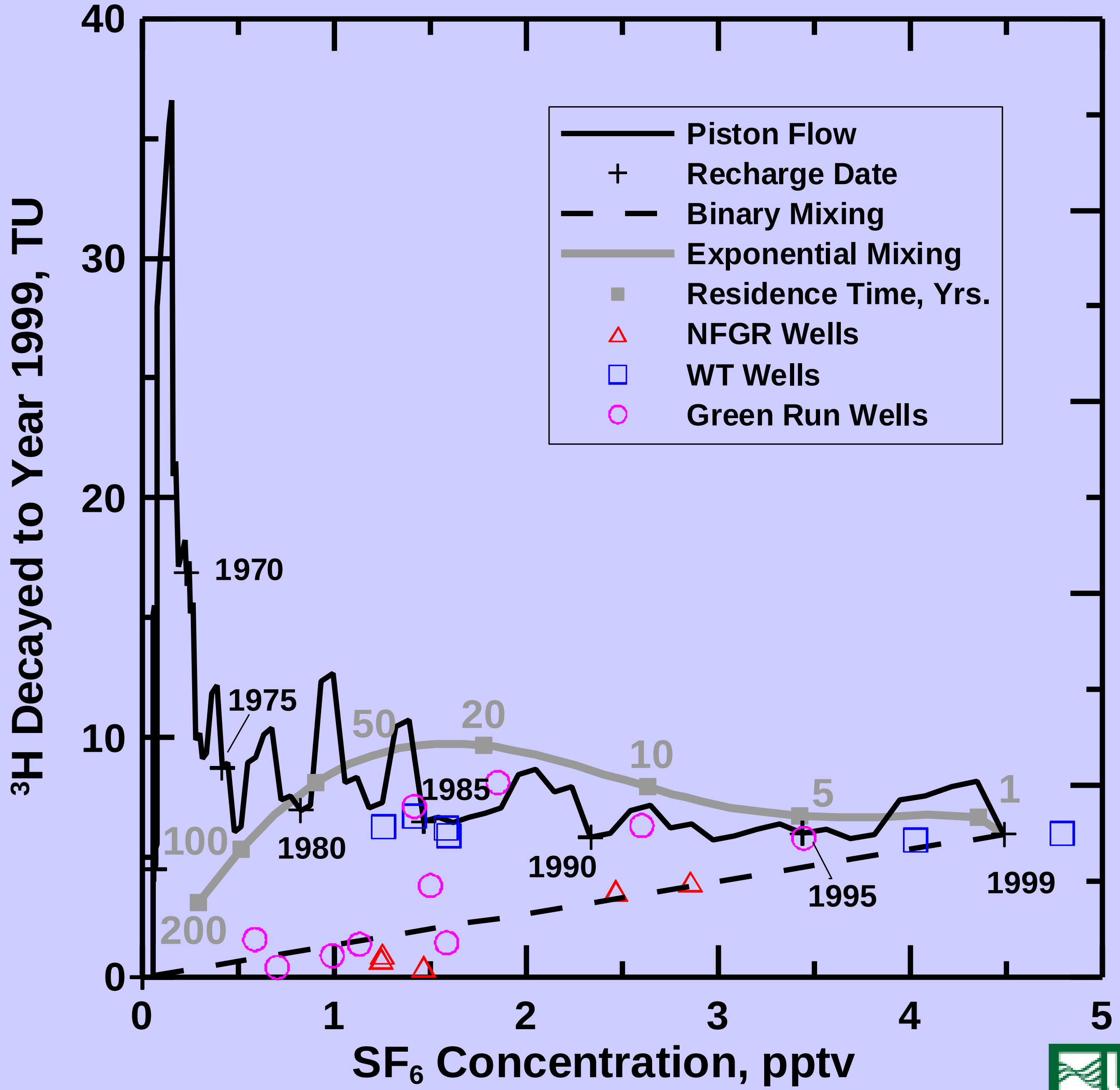
Piston Flow
Recharge Date
Binary Mixing
Exponential Mixing
Residence Time, Yrs.
CFC-113 Concentration, pptv
SF6 Concentration, pptv
0
40
80
120
0
1
2
3
4
5
1970
1975
1980
1985
1990
1995
1999
1
5
10
20
50
100
200



600
400
200
0
0
1
2
3
4
5
CFC-12 Concentration, pptv
SF6 Concentration, pptv
1970
1975
1980
1985
1990
1995
1999
1
5
10
20
50
100
200
Piston Flow
Recharge Date
Binary Mixing
Exponential Mixing
Residence Time, Yrs.
USGS



Piston Flow
Recharge Date
Binary Mixing
Exponential Mixing
Residence Time, Yrs.
1970
1975
1980
1985
1990
1995
1999
20
10
5
1
50
100
200
40
30
20
10
0
0
1
2
3
4
5
^3H Decayed to Year 1999, TU
SF_6 Concentration, pptv



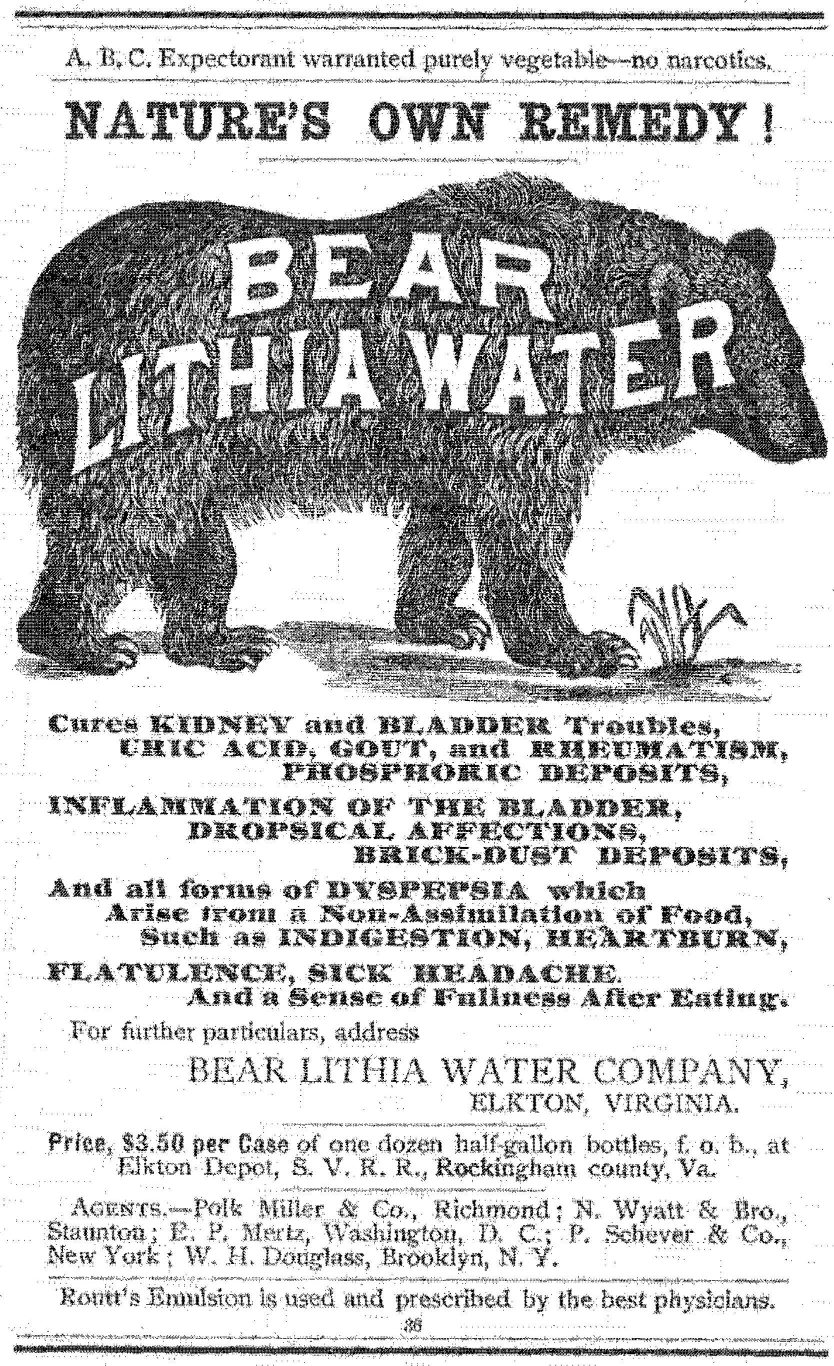
Piston Flow
Recharge Date
Binary Mixing
Exponential Mixing
Residence Time, Yrs.
NFGR Wells
WT Wells
Green Run Wells
1970
1975
1980
1985
1990
1995
1999
200
100
50
20
10
5
1
0
10
20
30
40
0
1
2
3
4
5
^3H Decayed to Year 1999, TU
SF_6 Concentration, pptv

Bear Lithia Spring (9/2/99)

Piston-Flow Ages
CFC-11   27.2 yrs
CFC-12   27.2 yrs
CFC-113 >Modern (100 pptv)
$^3H/^3He$ 30.0 yrs

Agreement in ages suggests
Piston flow (30 yrs in pipe flow).

Major Contradiction:
Tritium = 1.2 ± 0.2 TU
1969.6 water contained
about 130 TU; decays to 25 TU



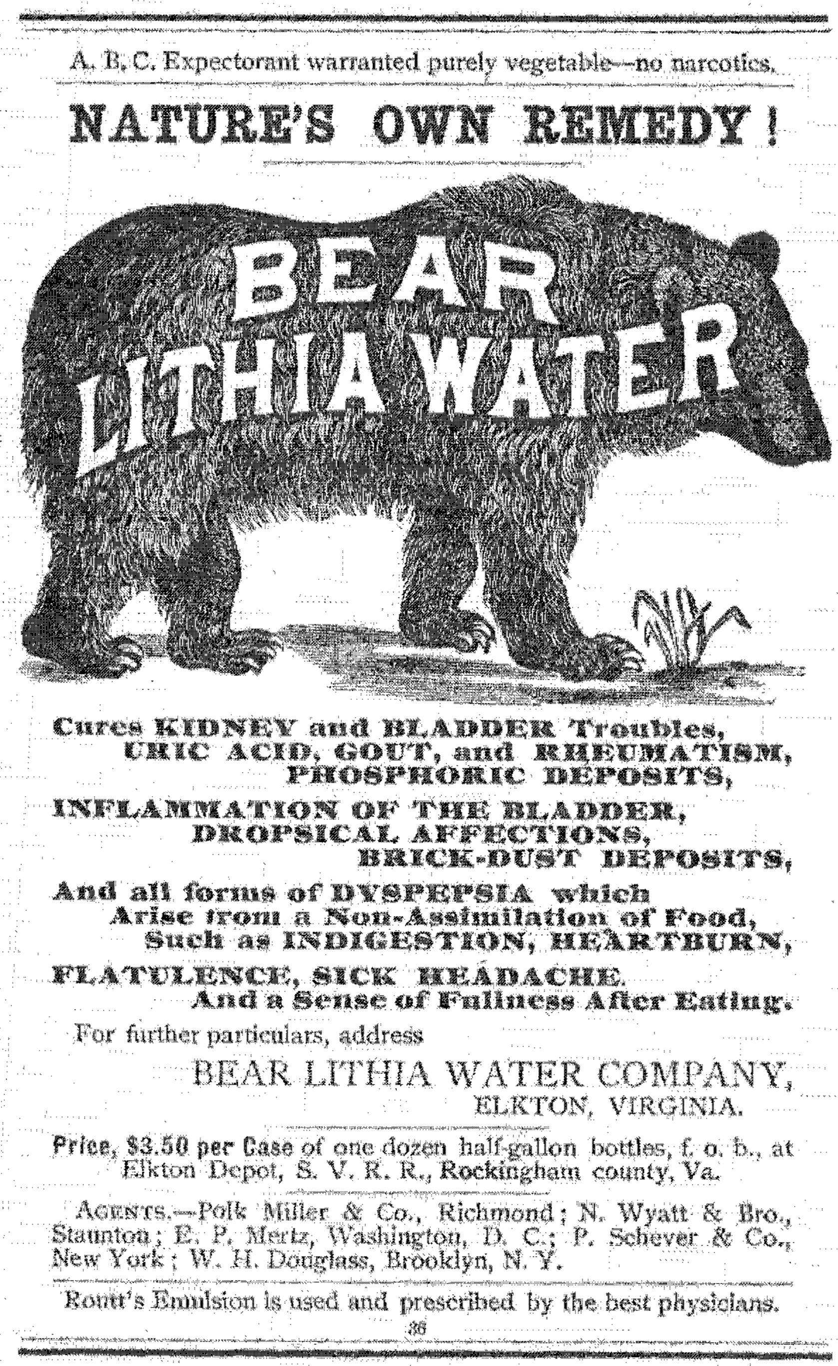
Bear Lithia Spring (9/2/99)

If we believe the $^3H/^3He$ age:

^3H = 1.2 TU
^3He(tritiogenic) = 5.2 TU
Initial ^3H = 1.2 + 5.2 = 6.4 TU

1969.6 precipitation = 130 TU

Samples contains only about 5% 1969.6 water.



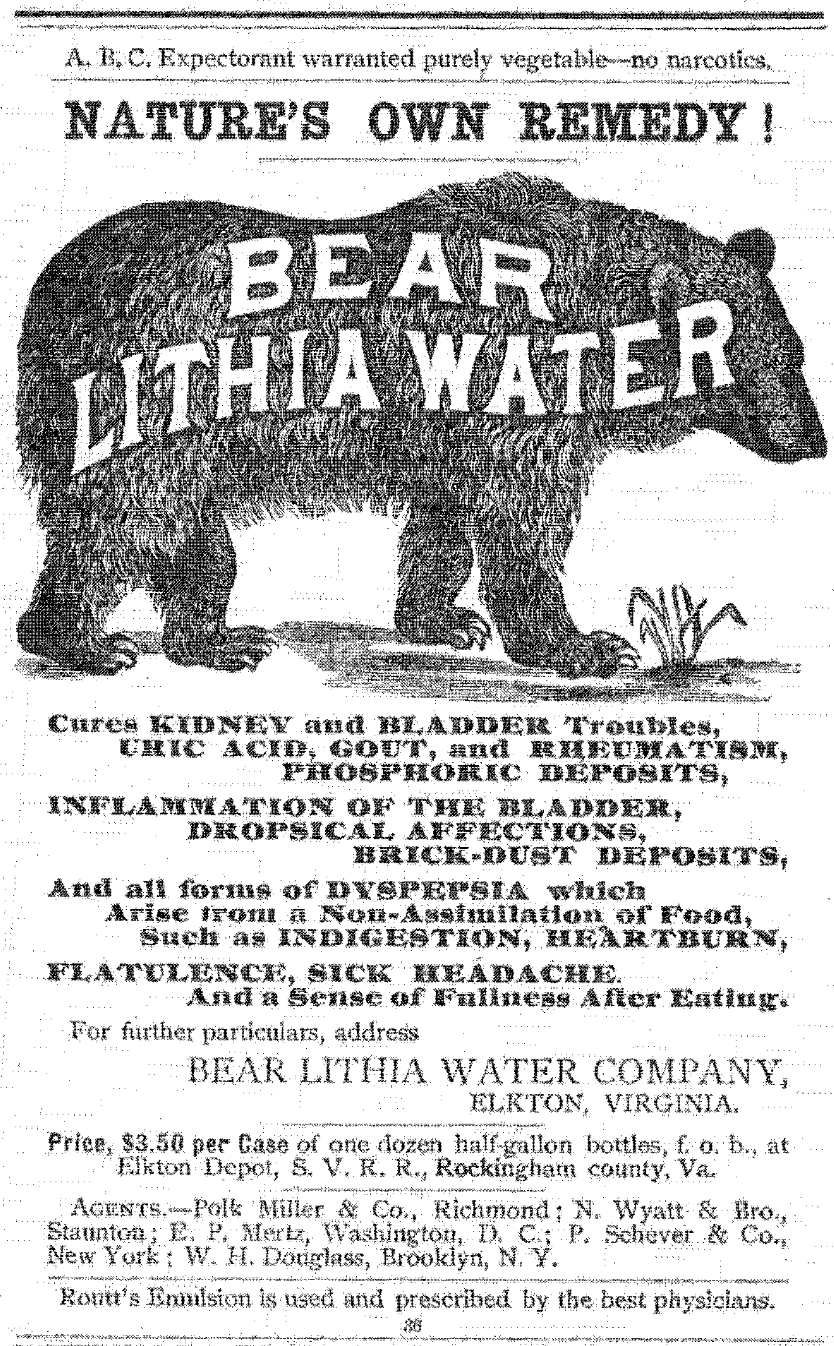
Bear Lithia Spring (9/2/99)

Implies CFC-11 and CFC-12 uniquely contaminated.

5% of 1970 air gives:
CFC-11 2.9 pptv
CFC-12 6.4 pptv

Measured:
CFC-11 87.9 pptv
CFC-12 176.1 pptv

Very unusual to have CFC-11 and CFC-12 contaminated in such a way to give identical piston-flow ages.



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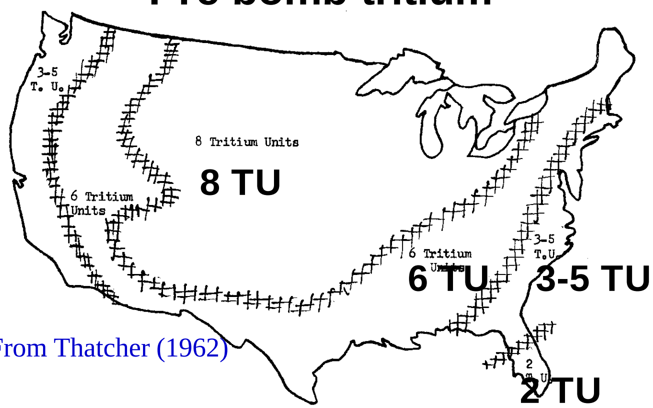
Bear Lithia Spring (9/2/99)

Is something wrong with the $^3H/^3He$ age?

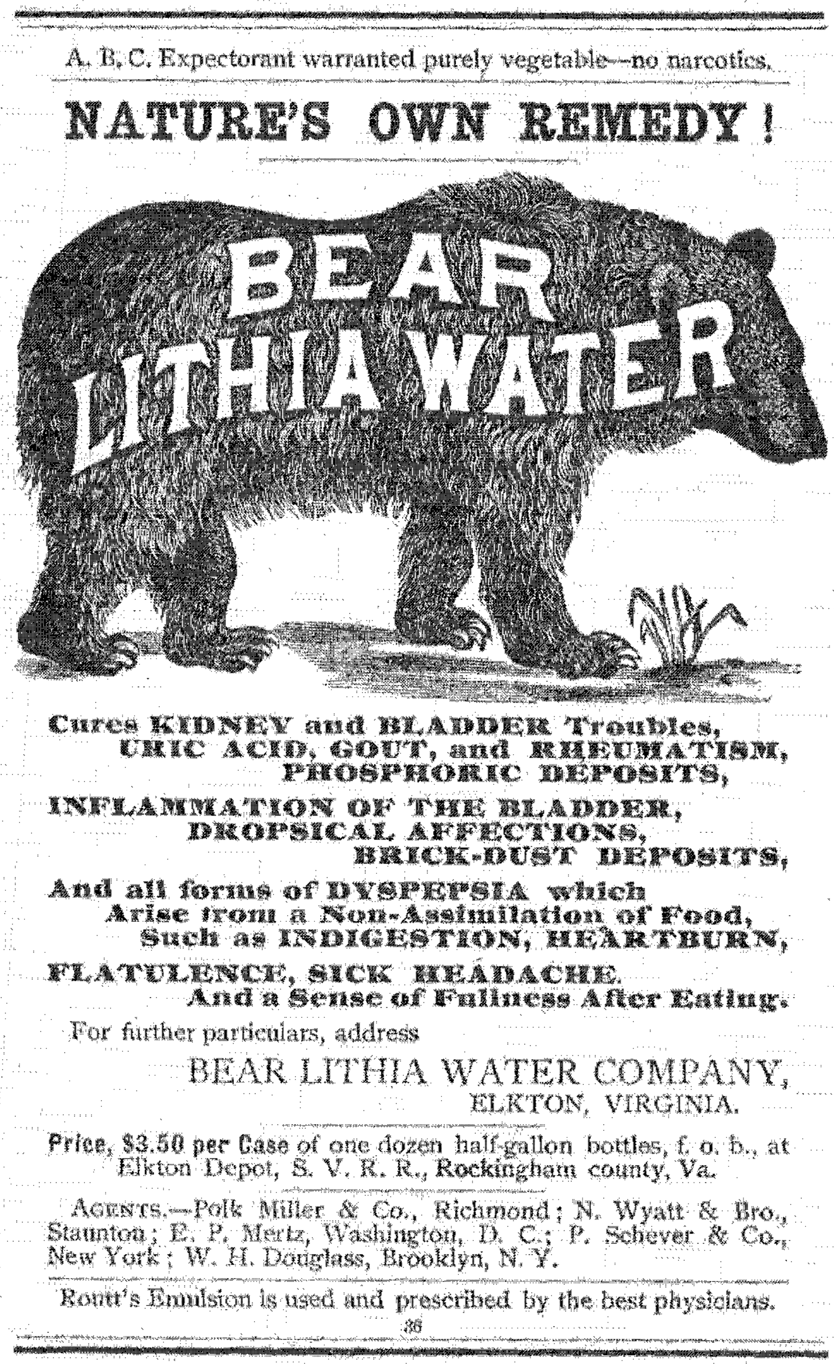
Pre-bomb tritium



From Thatcher (1962)

Fig. 2 — Suggested Variation of Natural Tritium Levels.

Sample contains > 90% pre-bomb water; Assumption that pre-bomb tritiogenic ^3He=0 may not be valid



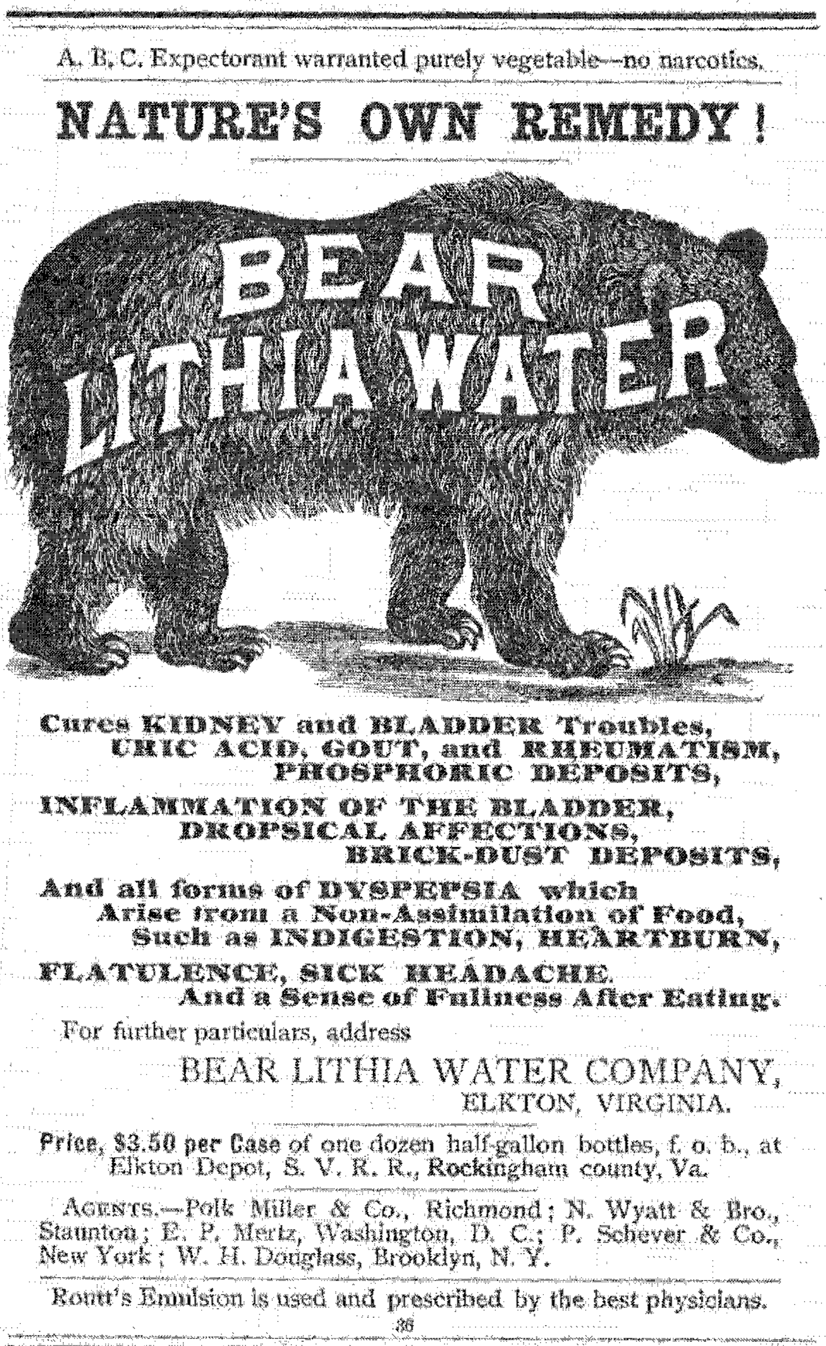
Bear Lithia Spring (9/2/99)

Correcting for assumed pre-bomb tritiogenic ^3He, young fraction varies from 5% at 30 yrs to 12% at 0 yrs age.

From CFC-11: 33.0 % 0 yrs water.
From CFC-12: 32.8 % 0 yrs water.

Implies ^3H should have been around 3 TU instead of 1.2 TU.

CONCLUSION: Discharge 67-88 % pre-bomb water mixed with approx. 12-33% modern water.



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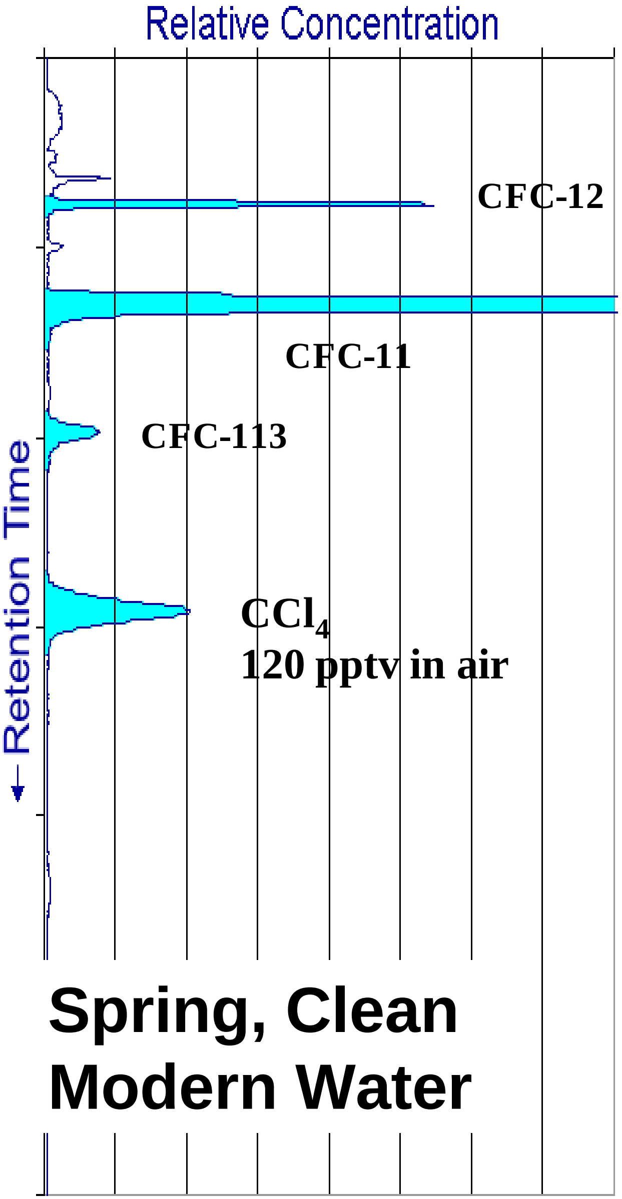
Susceptibility Determination

- **Tracer is Present:** Water discharged from the well is susceptible to contamination from anthropogenic inputs.
- **Tracer is "Absent":** Water discharged from the well is less susceptible to contamination from anthropogenic inputs. (Can never prove that the source is not susceptible– lower and lower detection limits)

GC-ECD Chromatograms

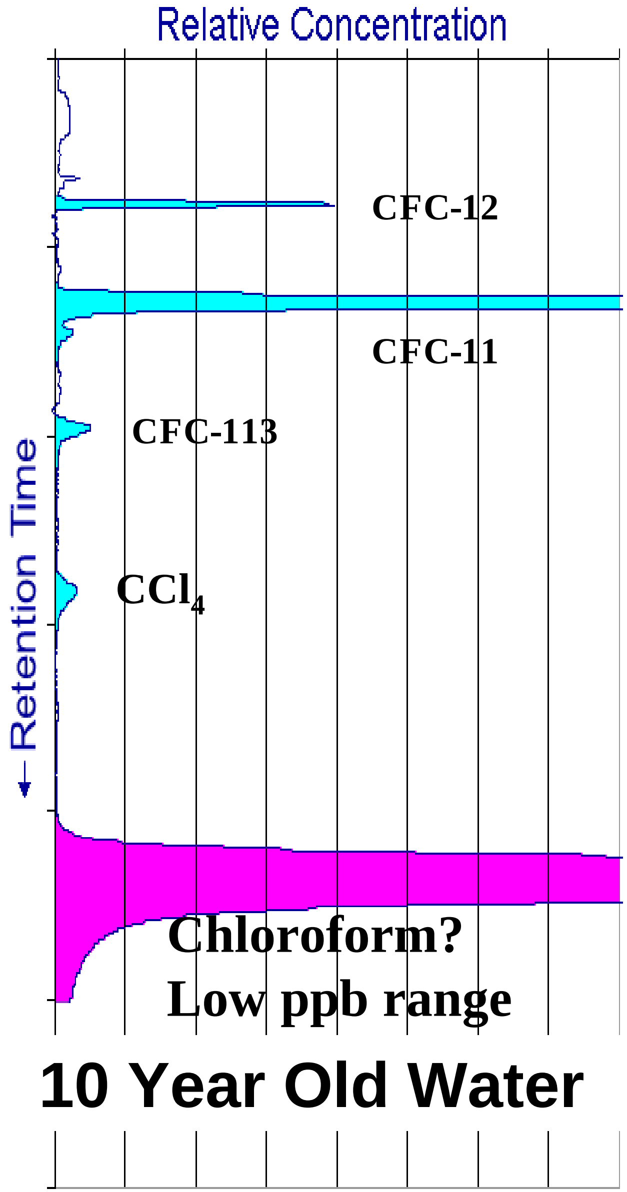
- Analysis by GC-ECD: Purge and trap gas chromatography with electron-capture detector.
- Detects halogenated VOCs (examples: CFCs, CCl_4, Halons, TCE, TCA, etc.
- Traditional analysis: GC-MS < 0.1 ug/L (= 100 ng/L = 100,000 pg/L)
- GC-ECD: < 1 pg/L (= 5 orders of magnitude below normal reporting levels)

Shenandoah National Park
Spring
Drinking Water
Modern Clean Water



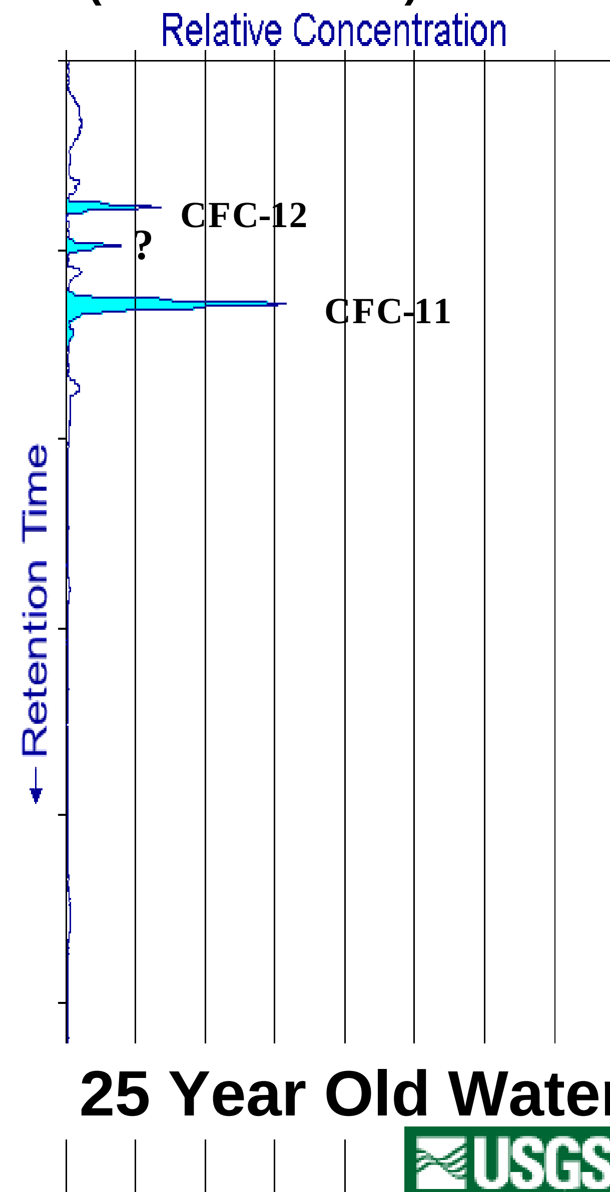
Spring, Clean Modern Water

Spring
Yorktown, VA
Drinking Water



10 Year Old Water

Fort Wainright
Fairbanks, AK
(Air Force Base)



25 Year Old Water

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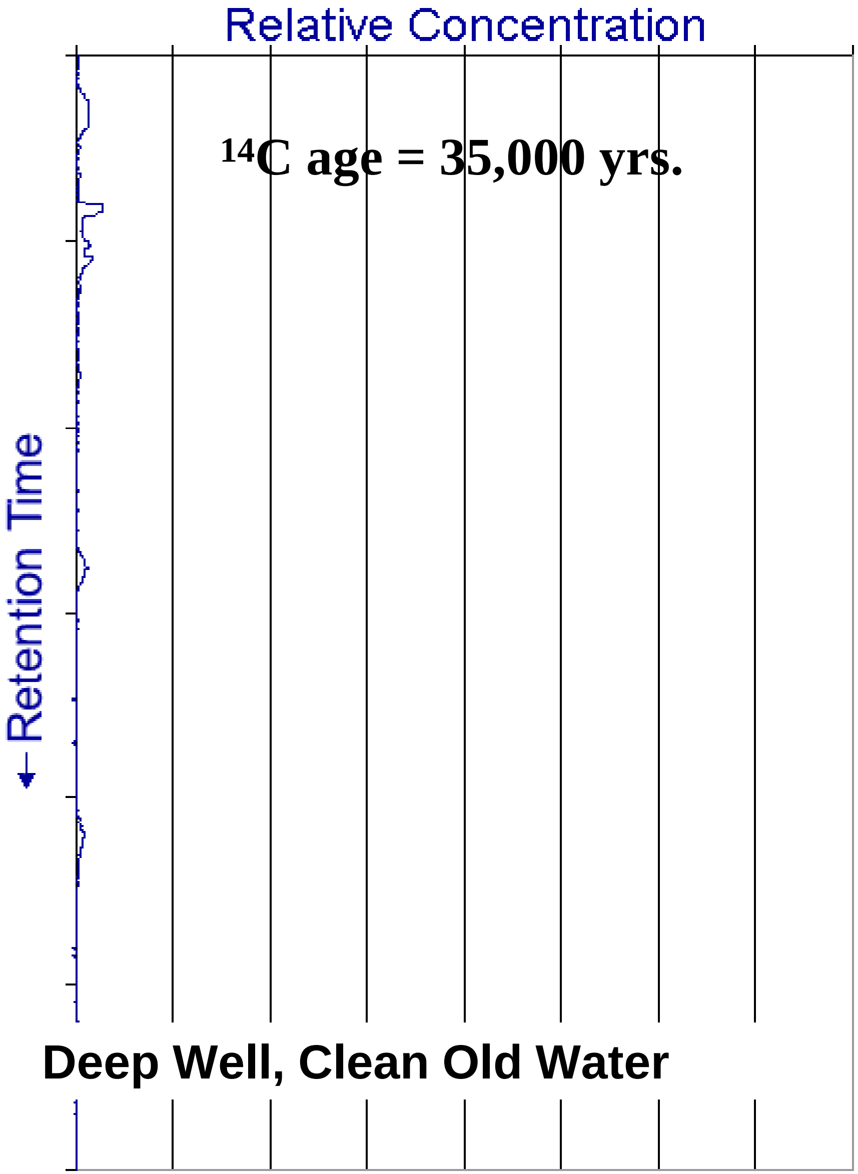
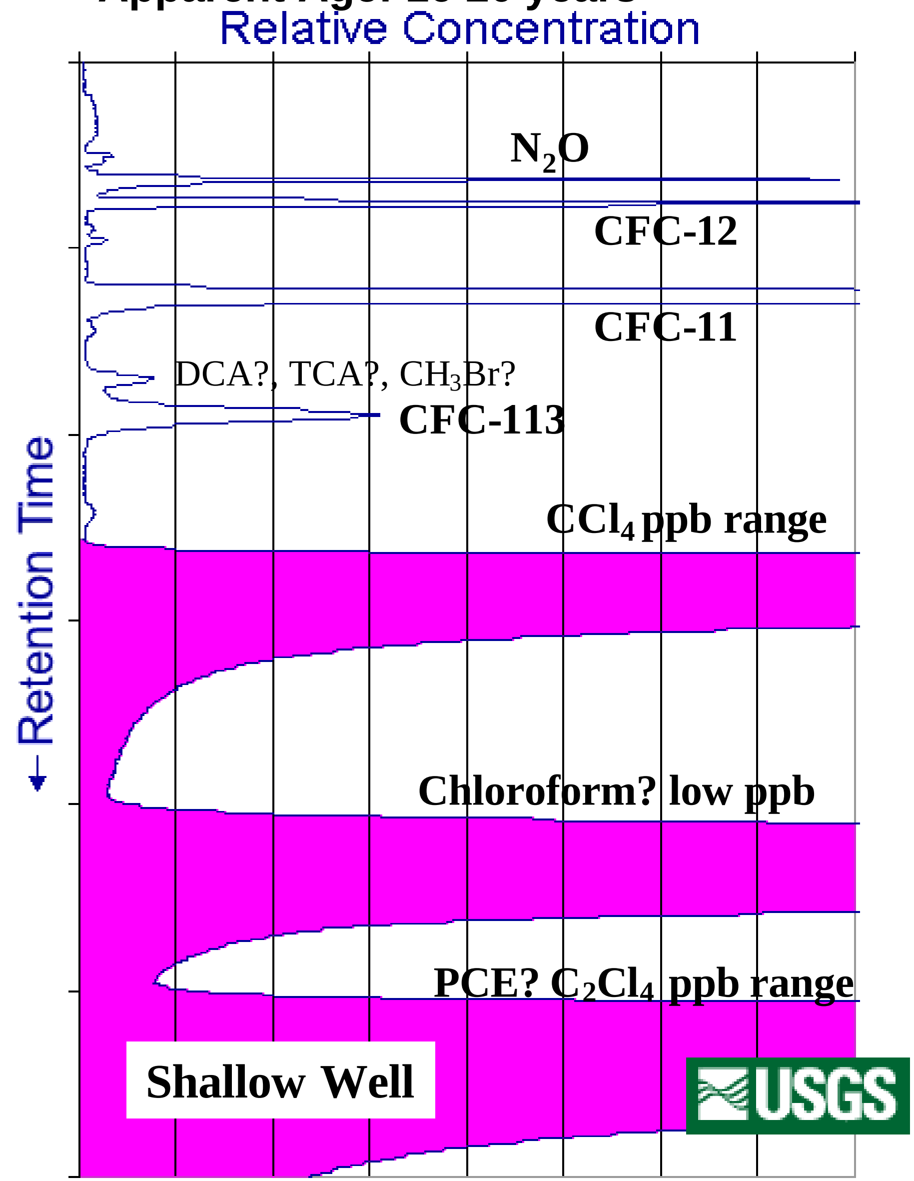
A Town well in VA
Depth: 135 (125-136) meters
Drinking Water Well
Atlantic Coastal Plain
Water Greater than 60 Years old

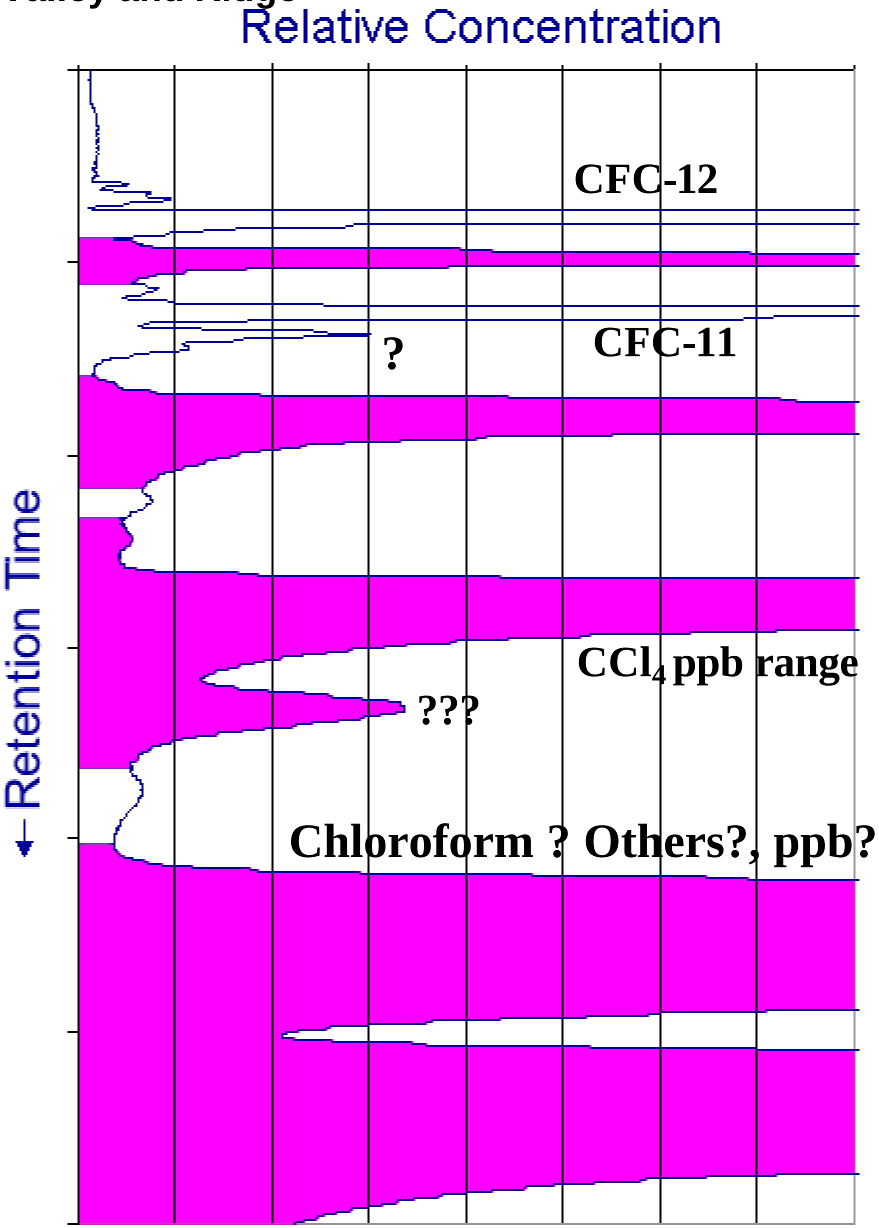


A Town well in VA
Depth: 18 (13-18) meters
Drinking Water Well
Atlantic Coastal Plain
Apparent Age: 16-20 years



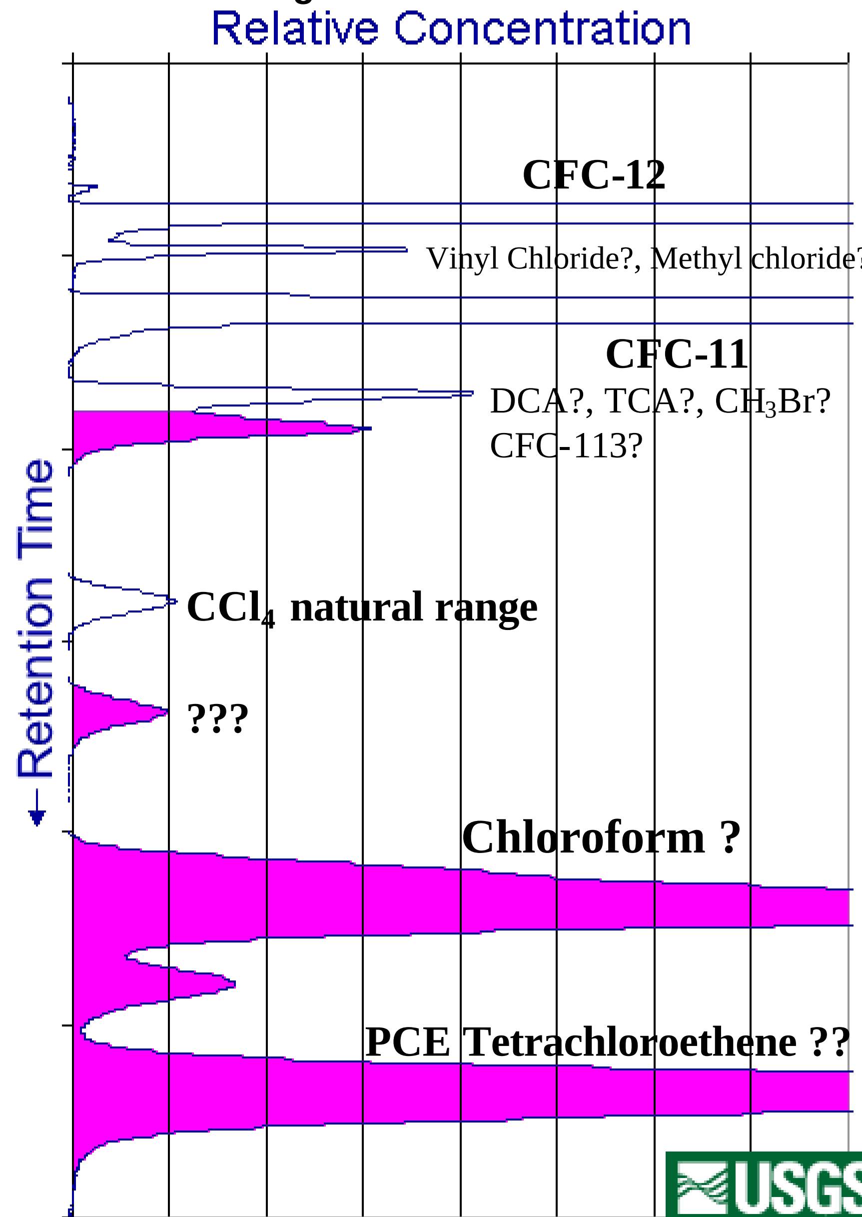
A Town well in VA

Drinking Water Well
Depth: 190 meters
Valley and Ridge



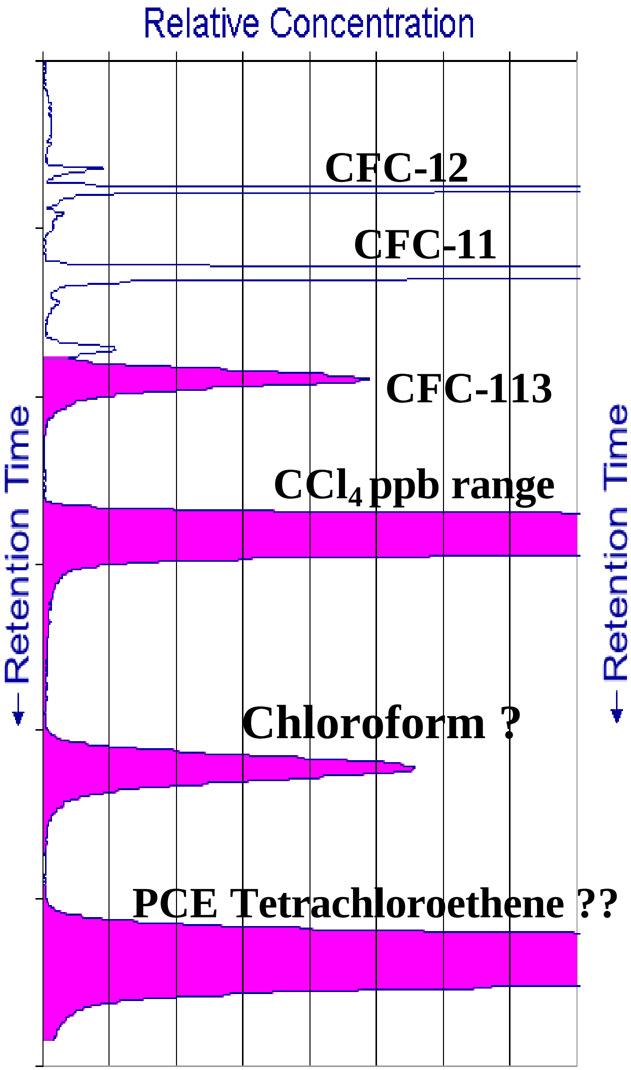
A Town well in VA

Drinking Water Well
Depth: 115 meters
Blue Ridge



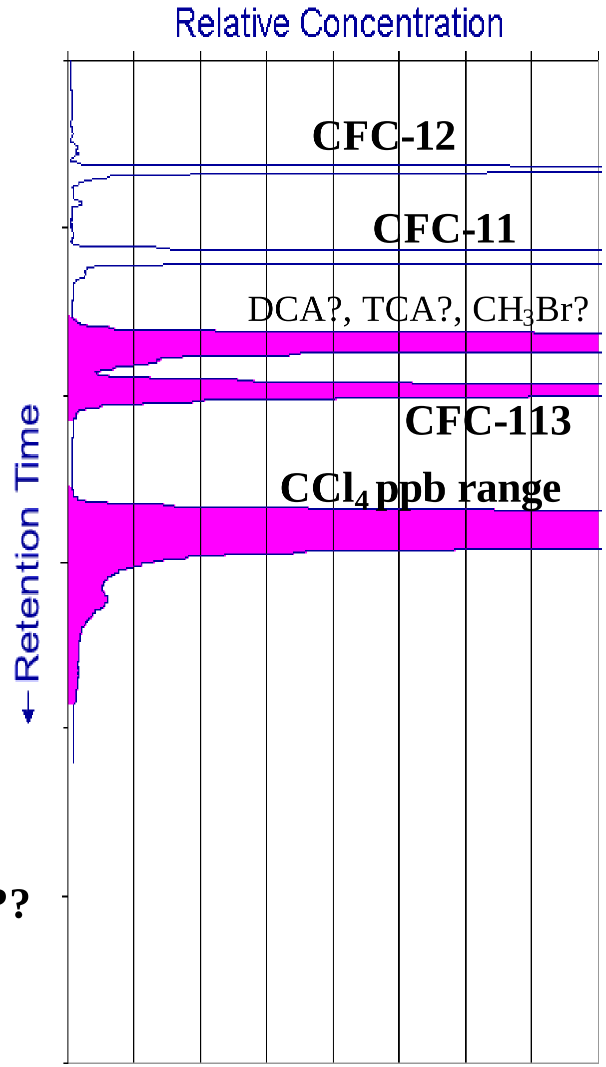
A Town well in VA

Drinking Water Well
Depth: 186m
Blue Ridge



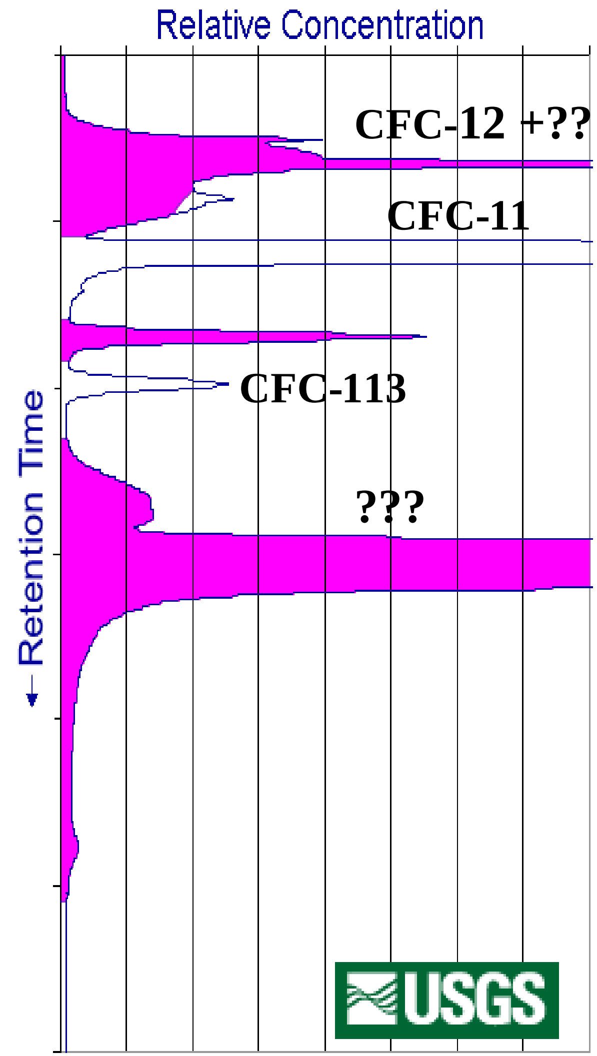
A Town well in VA

Drinking Water Well
Depth: 85m
Blue Ridge



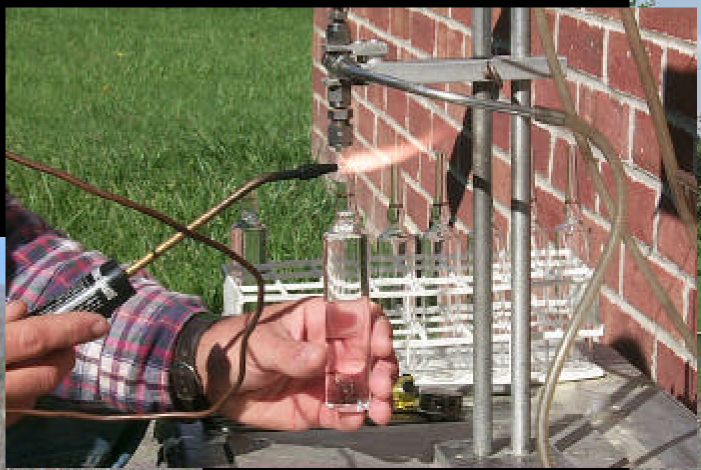
A Town well in VA

Drinking Water Well
Depth: 122m
Piedmont



Aquifer Susceptibility in Virginia, 1998-2000

Nelms, D.L. and others,
2003, USGS
WRIR 03-4278



http://water.usgs.gov/pubs/of/2003/ofr03-246/ofr03-246.htm

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Regional aquifer systems and sample locations

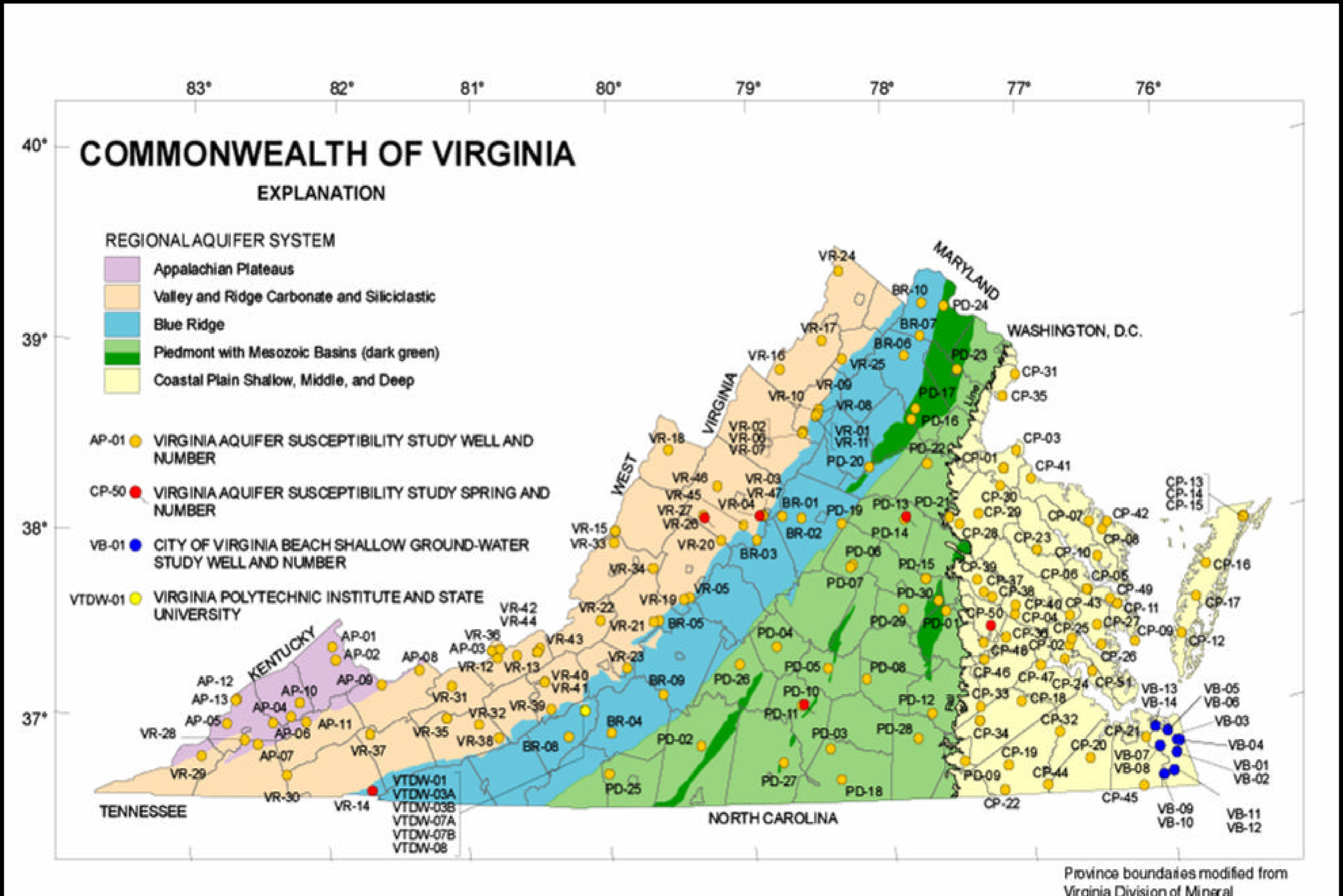

Figure 1. Location of wells and springs sampled in Virginia, 1998-2000.

Apparent age of young water fraction

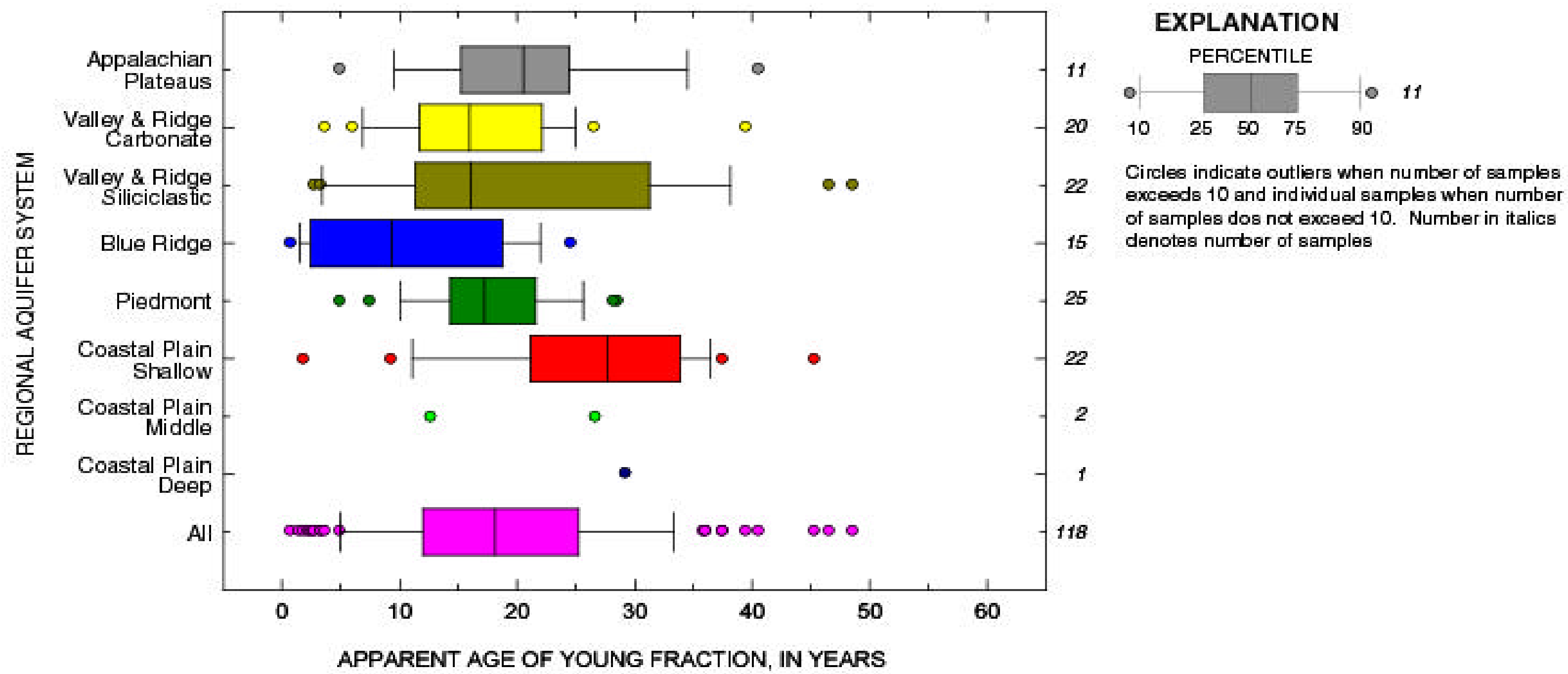

Figure 6. Distribution of apparent age of young fraction in binary mixtures with old (pre-chlorofluorocarbon) waters by regional aquifer system.

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Percentage of young water fraction

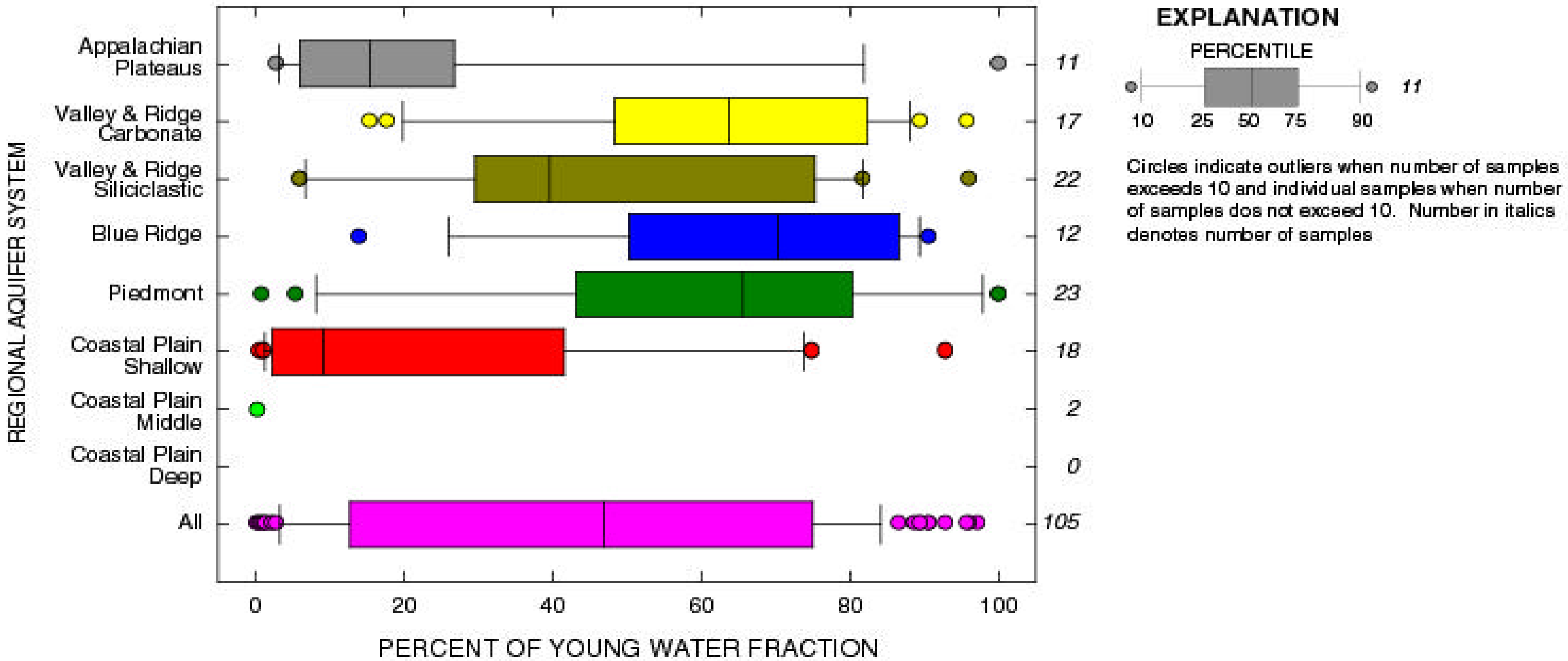

Figure 7. Distribution of young water fraction in binary mixtures with old (pre-chlorofluorocarbon) waters by regional aquifer system. Numbers in italics indicate number of samples.

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Percentage and apparent age of young water fraction

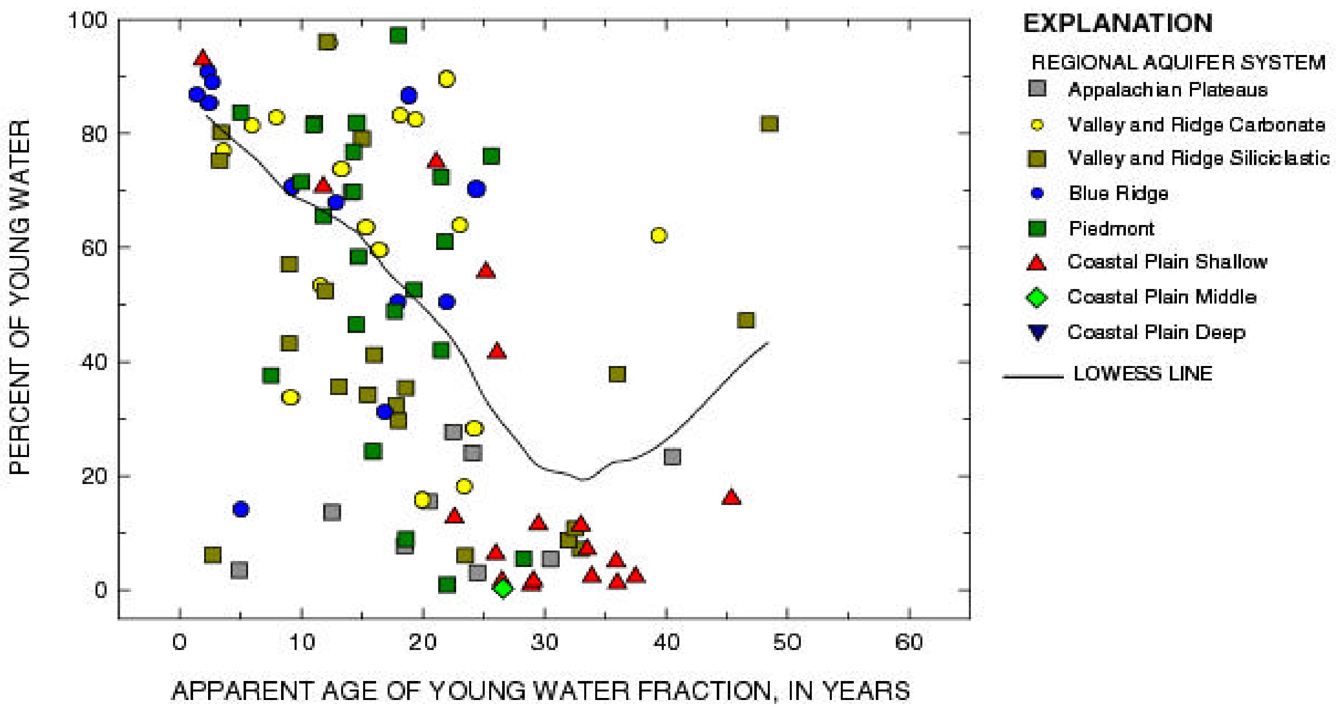

Figure 8. Comparison of percent and apparent age of young water fraction in binary mixtures with old (pre-chlorofluorocarbon) waters by regional aquifer system.

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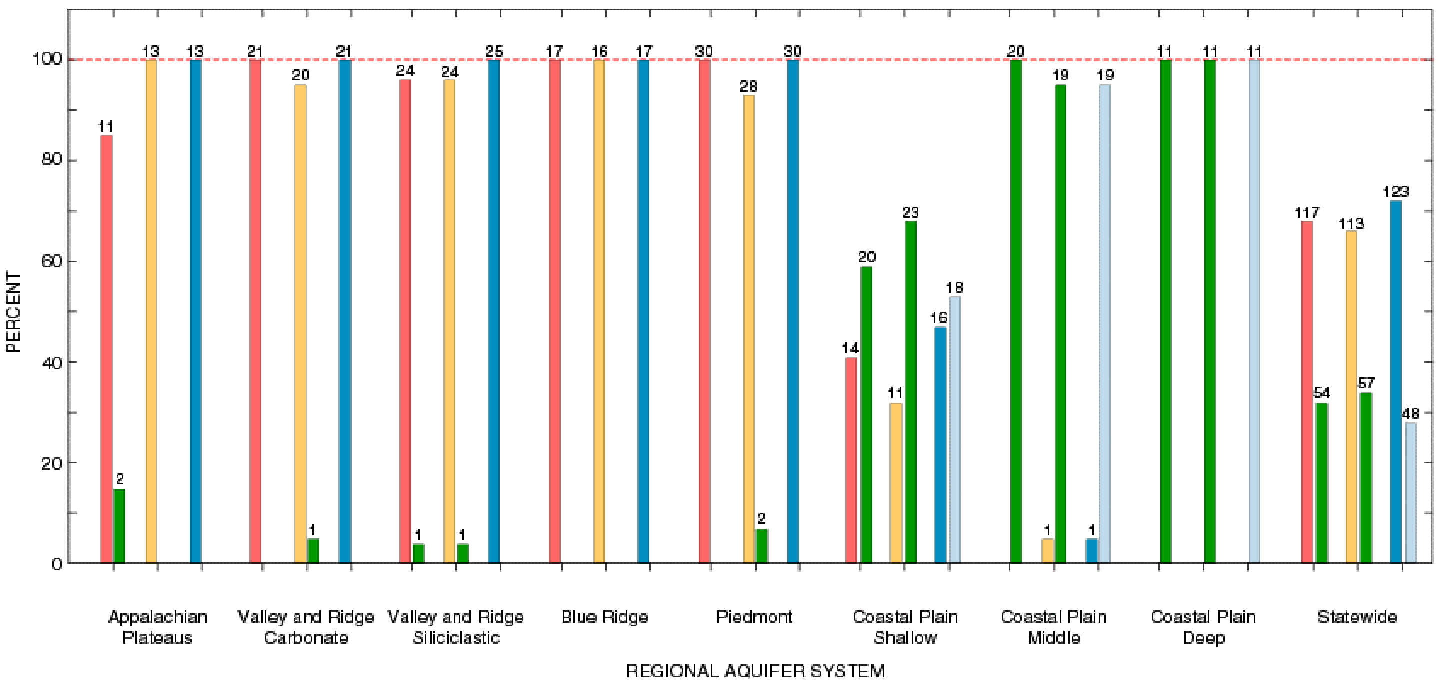
Exceedance of threshold CFC and tritium concentrations



Threshold Values

CFCs-- 5 pg/kg

Tritium-- 0.6 TU

EXPLANATION

THRESHOLD CHLOROFLUOROCARBON CONCENTRATION EXCEEDED

THRESHOLD TRITIUM CONCENTRATION EXCEEDED

THRESHOLD CHLOROFLUOROCARBON OR TRITIUM CONCENTRATION NOT EXCEEDED

SUSCEPTIBILITY DETERMINATION

SUSCEPTIBLE

NOT SUSCEPTIBLE

Figure 4. Exceedance of threshold chlorofluorocarbon and tritium concentrations and susceptibility determinations by regional aquifer system.

VOCs detections and susceptibility thresholds

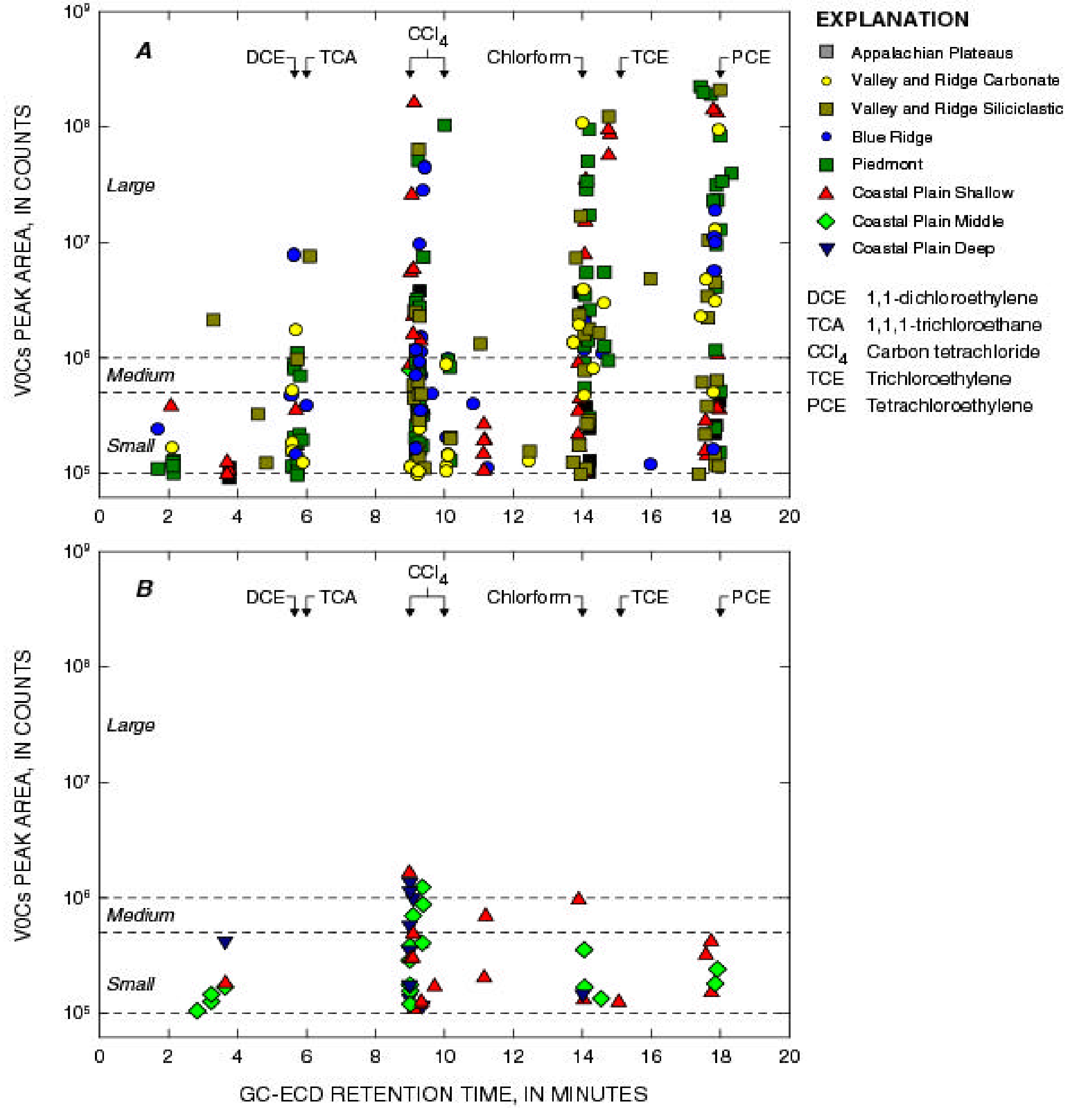


Figure 17. Comparison of peak areas and retention times for volatile organic compounds (VOCs) from gas chromatography with an electron capture detector (GC-ECD) analysis for samples that exceeded susceptibility threshold concentrations (*A*) and for samples that did not exceed susceptibility threshold concentrations (*B*). Data from Shapiro and others (2002).

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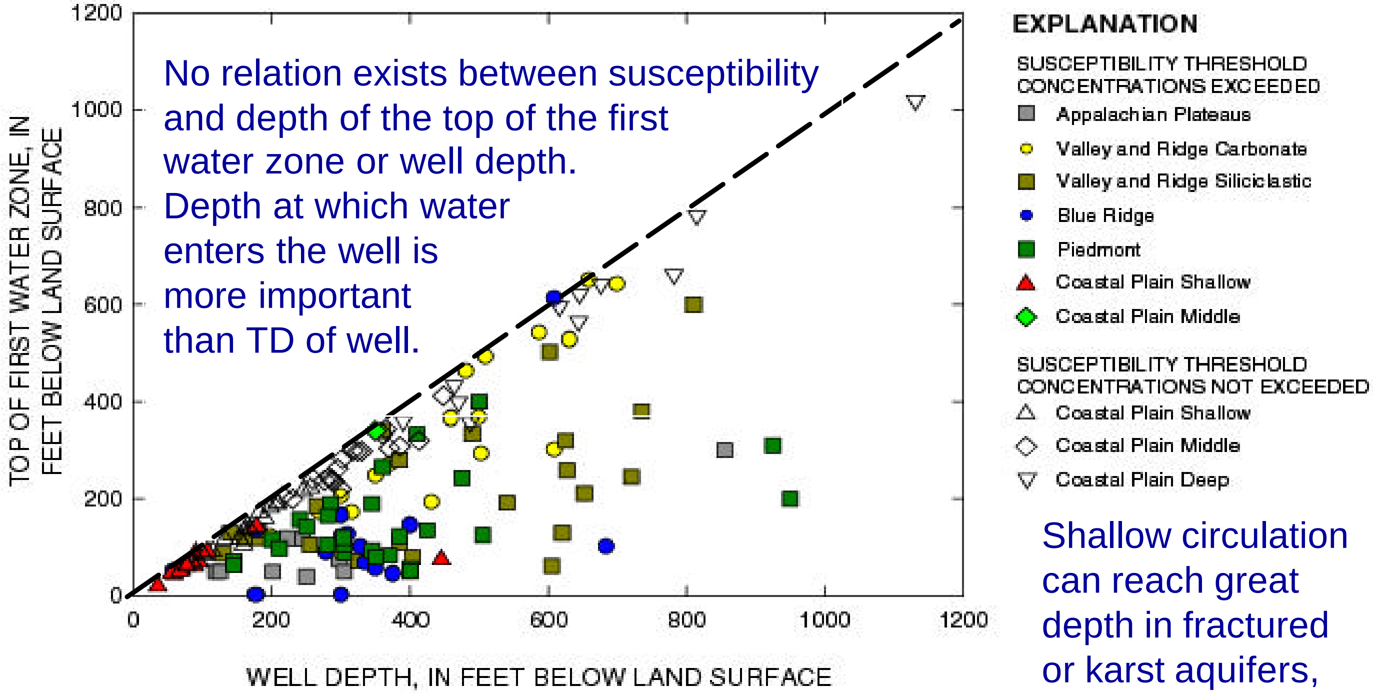
Susceptibility thresholds and depths



No relation exists between susceptibility and depth of the top of the first water zone or well depth. Depth at which water enters the well is more important than TD of well.

Shallow circulation can reach great depth in fractured or karst aquifers, due in part to pumpage.

Figure 19. Comparison of depth to top of first water zone and well depth to exceedance of susceptibility threshold concentrations by regional aquifer system.

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Degree of aquifer susceptibility

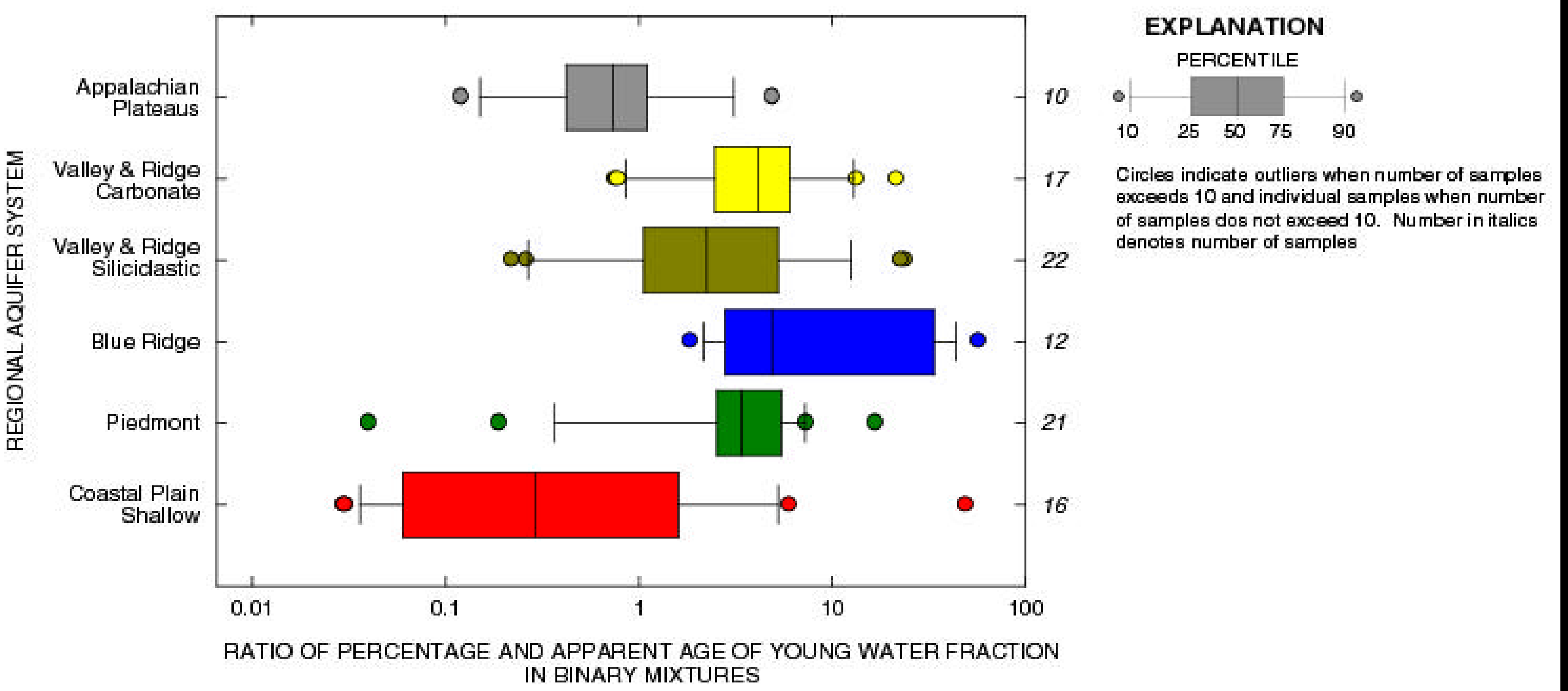

Figure 20. Distribution of the ratio of the percentage and apparent age of the young water fraction in binary mixtures with old (pre-chlorofluorocarbon) waters by regional aquifer system.

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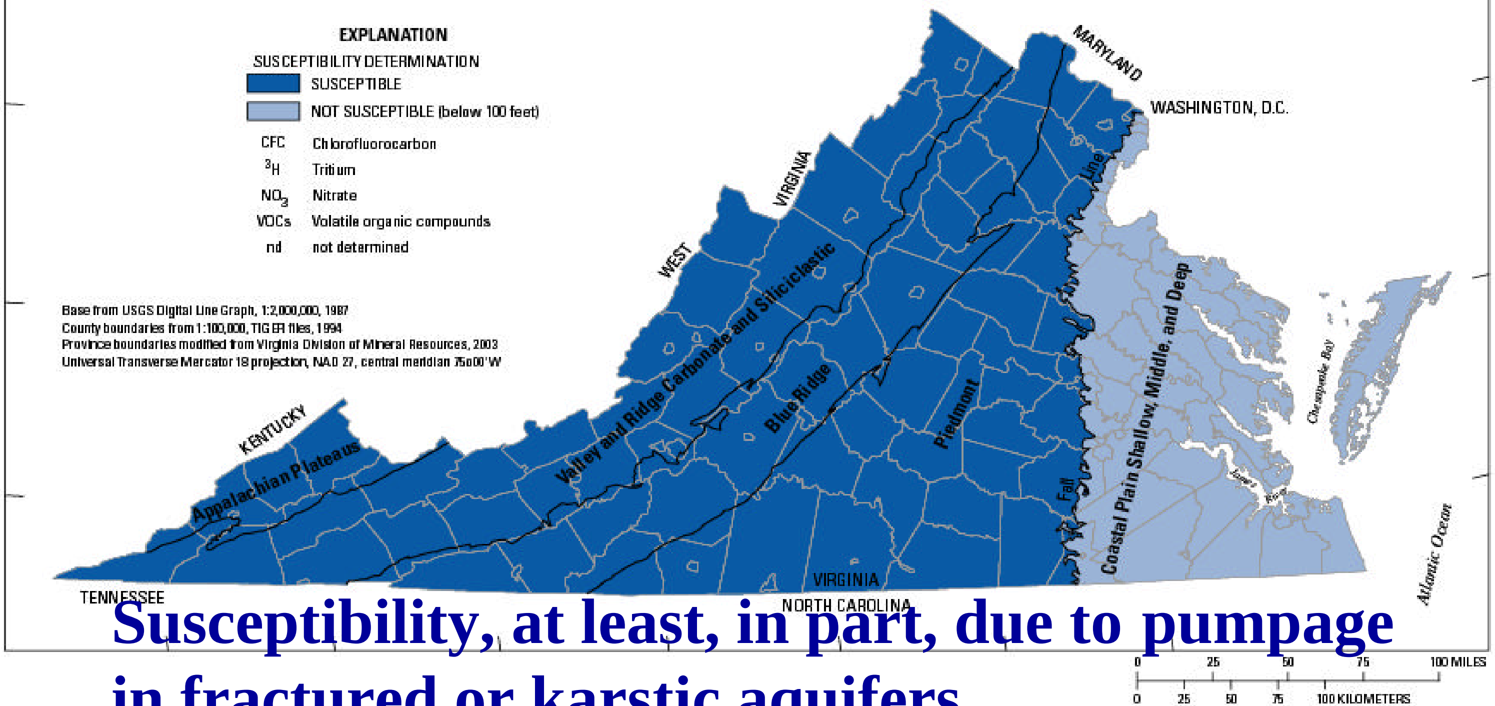
Aquifer Susceptibility in Virginia

Regional aquifer system	Exceedance, in percent: Threshold concentration CFC	Threshold concentration ^3H	Detection limit NO_3	Samples with CFC contamination, in percent	Samples with VOCs detected, in percent	Range: Apparent age[1] Young	Apparent age[1] Old	Percentage young water fraction	Susceptibility determination
Appalachian Plateaus	85	100	15	15	62	4.9 - 40.5	nd	3 - 100	Susceptible
Valley and Ridge Carbonate	100	95	90	62	67	3.6 - 39.5	nd	16 - 96	Susceptible
Valley and Ridge Siliciclastic	96	96	40	36	88	2.7 - 48.5	nd	6 - 96	Susceptible
Blue Ridge	100	100	65	59	94	0.8 - 24.5	nd	14 - 91	Susceptible
Piedmont	100	93	57	57	79	5.0 - 28.5	nd	0.9 - 100	Susceptible
Coastal Plain Shallow	41	32	32	12	71	1.9 - 45.4	2,420 - 10,100	.8 - 93	Susceptible (upper 100 feet)
Coastal Plain Middle	0	5	10	0	55[2]	nd	9,090 - 36,900	nd nd nd	Not Susceptible
Coastal Plain Deep	0	0	18	0	91[2]	nd	27,900 - 39,700	nd nd nd	Not Susceptible

[1] Apparent age of young waters in years. Apparent age of old waters in radiocarbon years.
[2] May be the result of analytical or sampling error, transient leakage from the well casing or wellbore, or remnants of well-construction or pump maintenance activities.

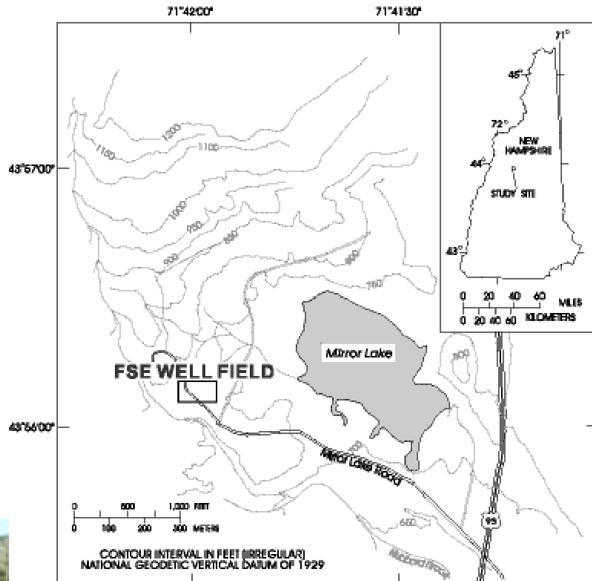


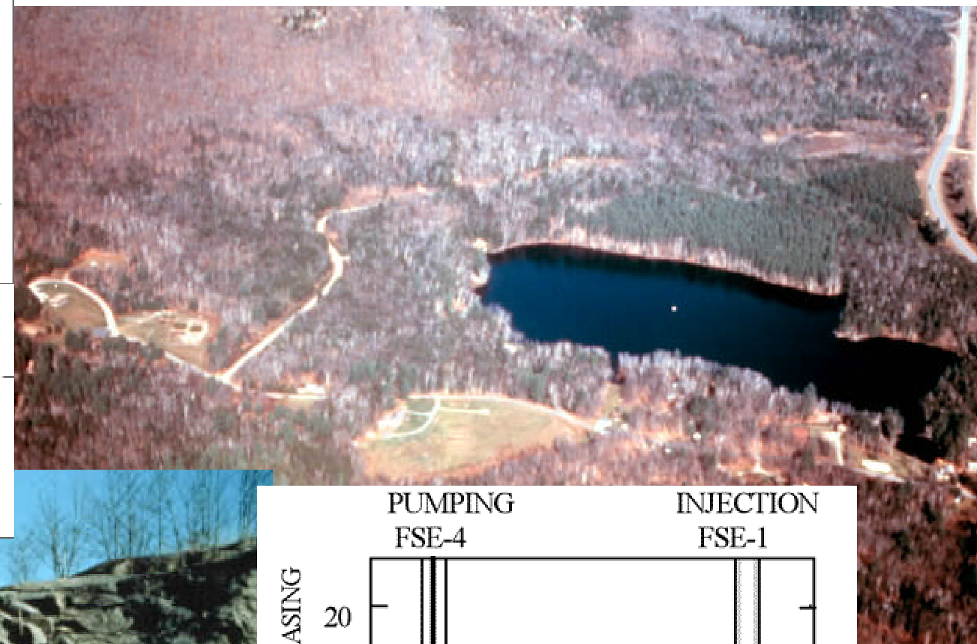
Susceptibility, at least, in part, due to pumpage in fractured or karstic aquifers.

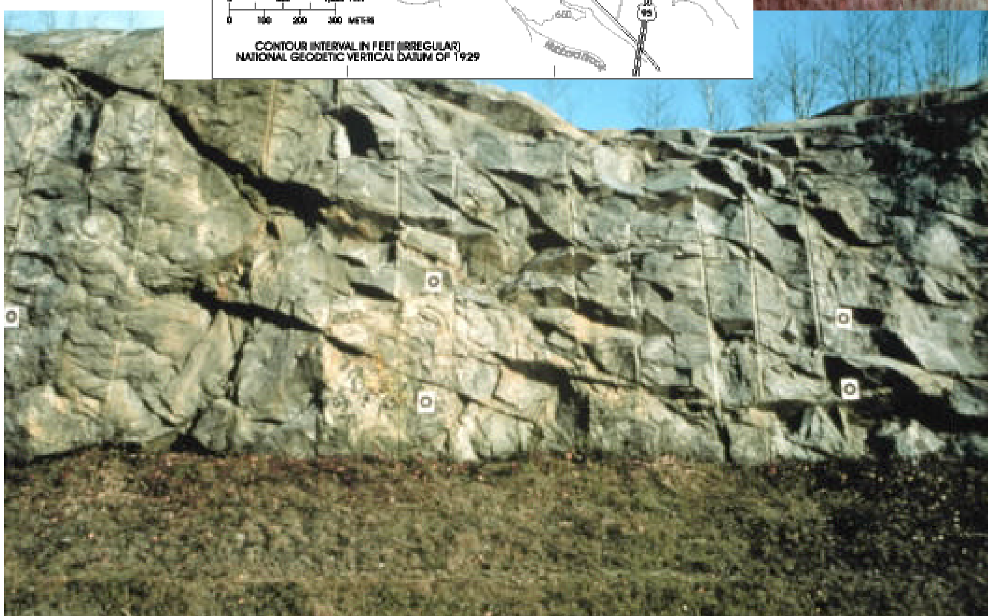
Figure 19. Susceptibility to contamination from near-surface sources of the regional aquifer systems in Virginia, 1998-2000.

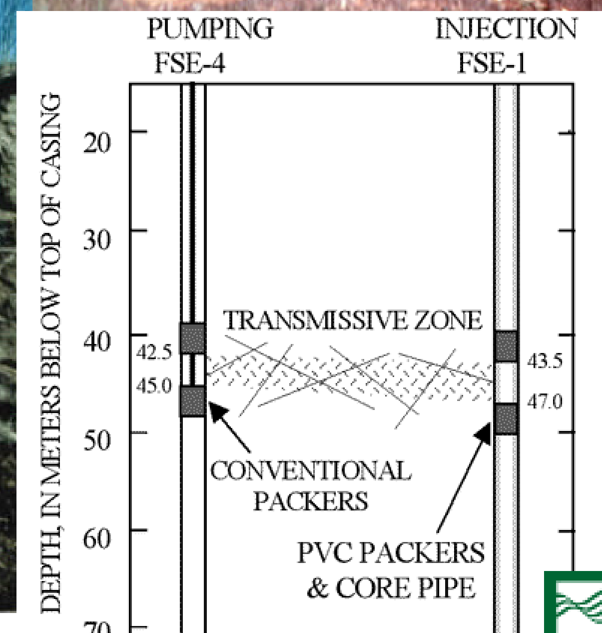
USGS science for a changing world

Fractured-rock aquifers near Mirror Lake, New Hampshire, have highly varied and complex hydrologic characteristics.



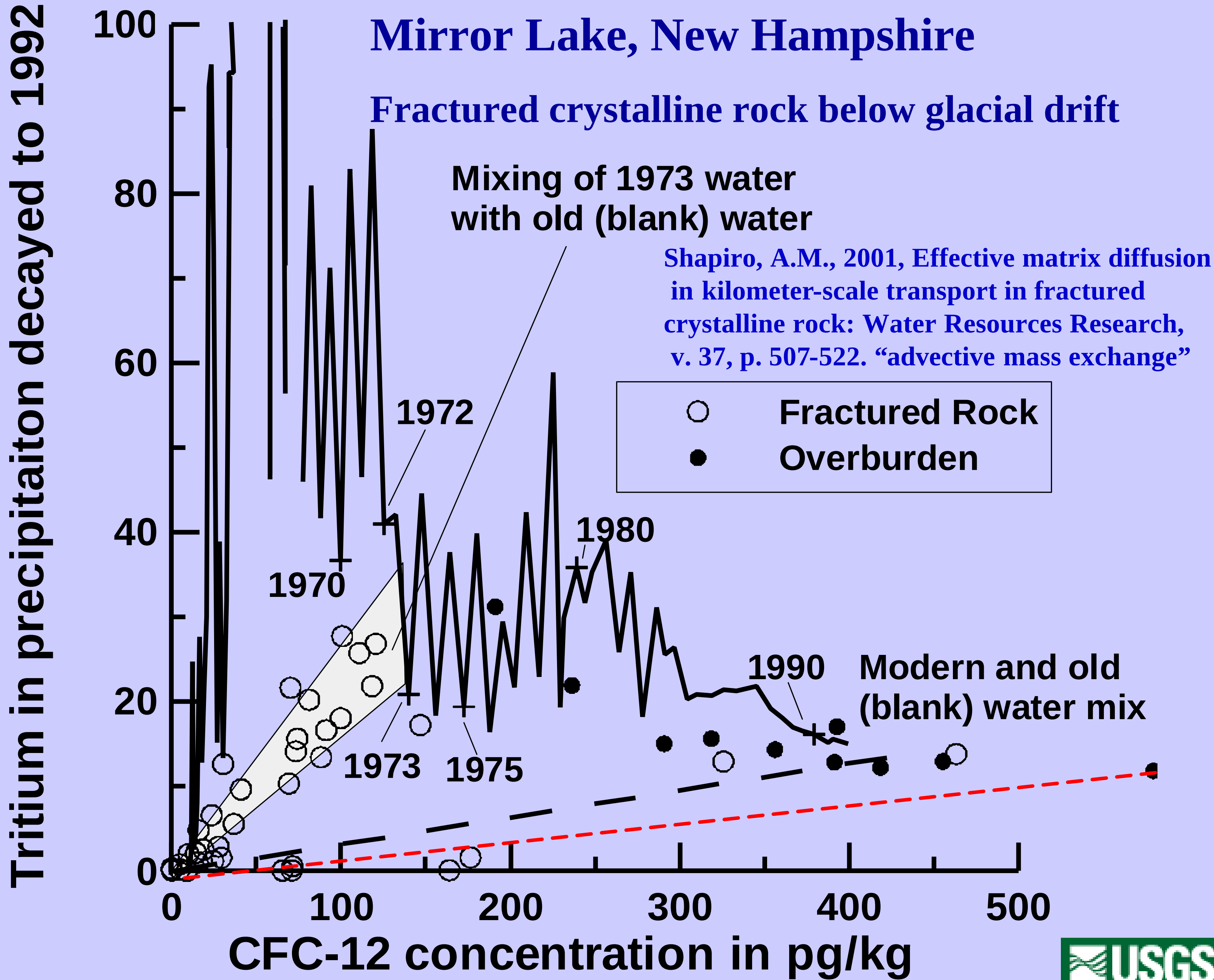






Mirror Lake, New Hampshire

Fractured crystalline rock below glacial drift



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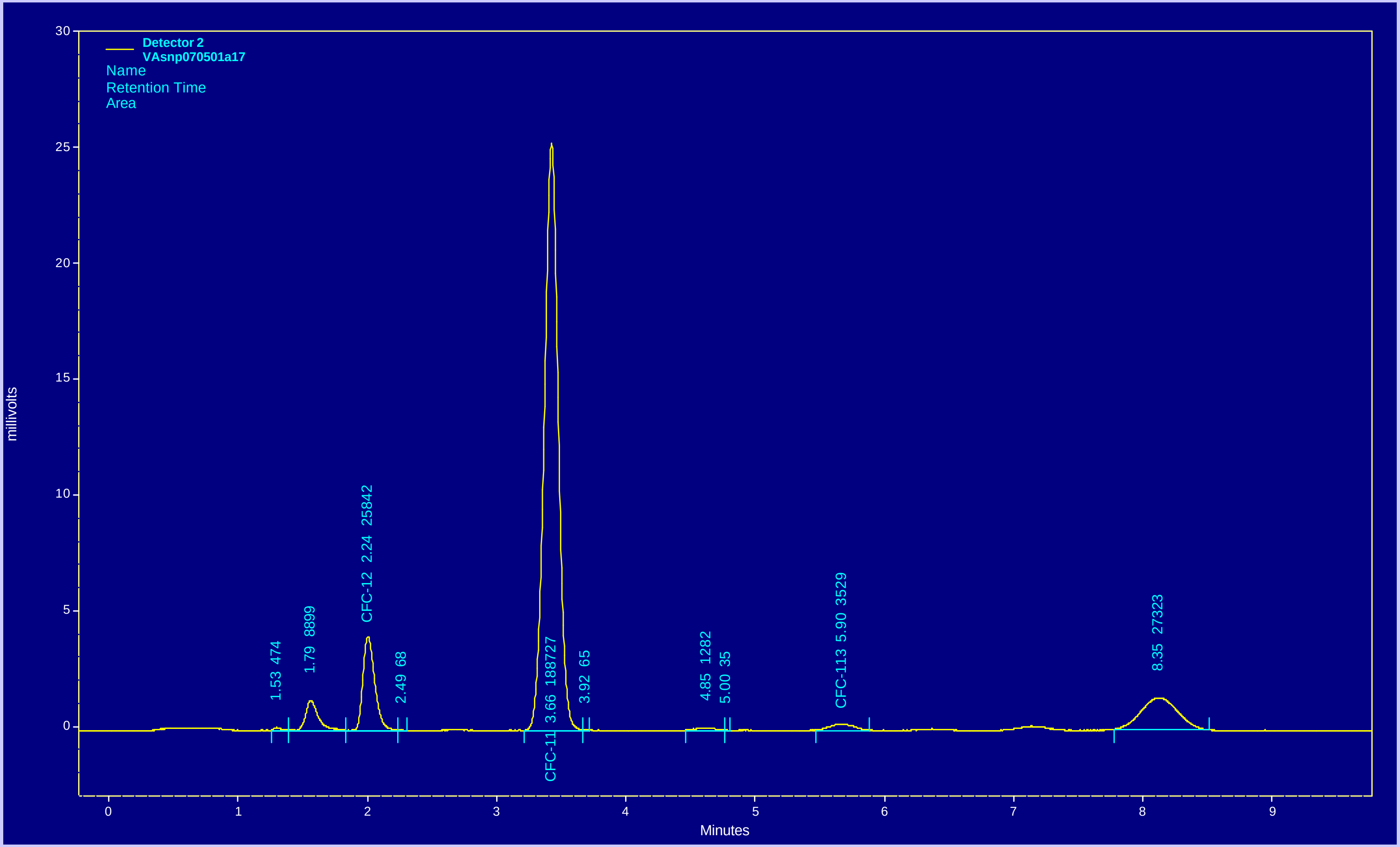
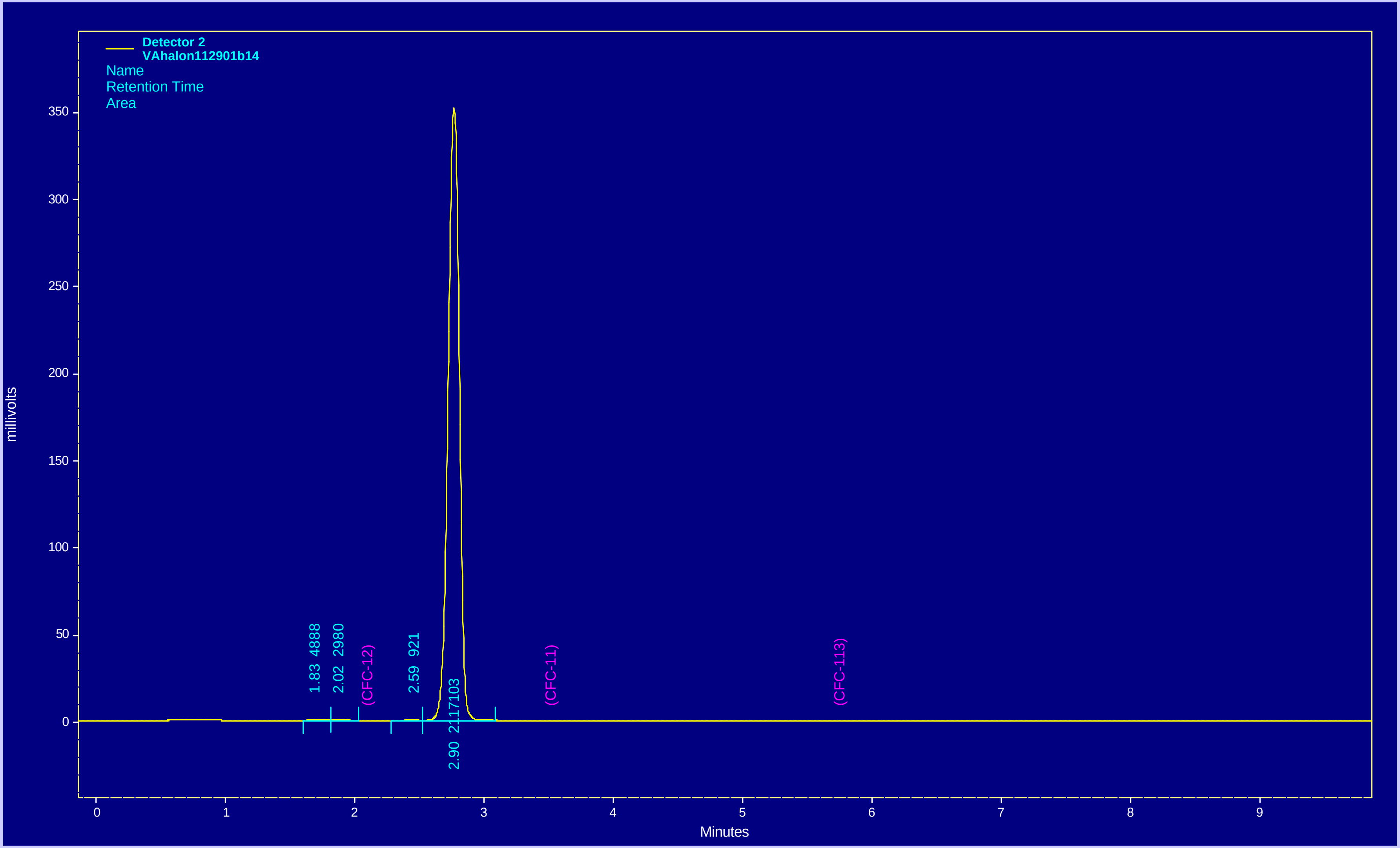
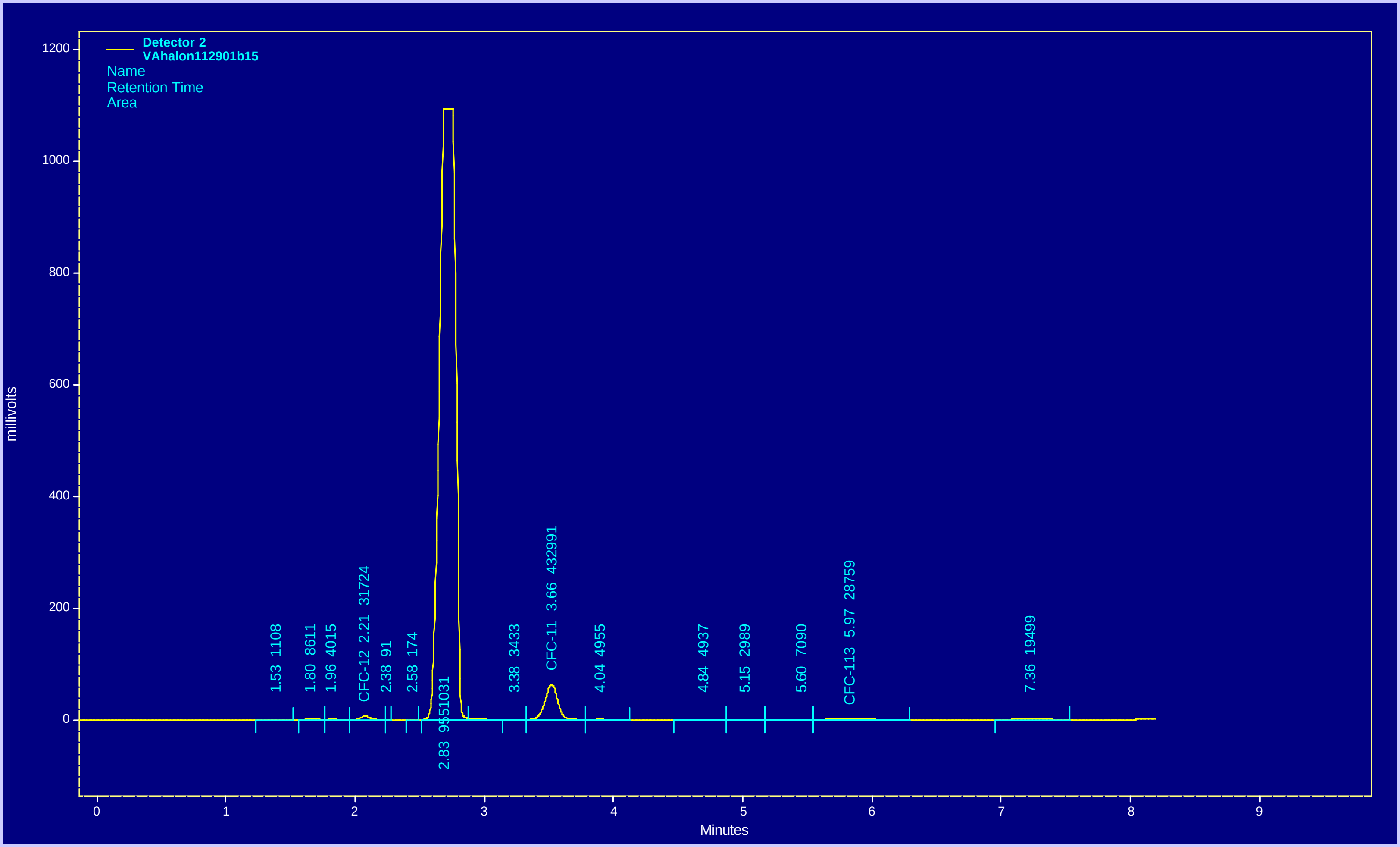
Halon 1211
Drilling Tracer



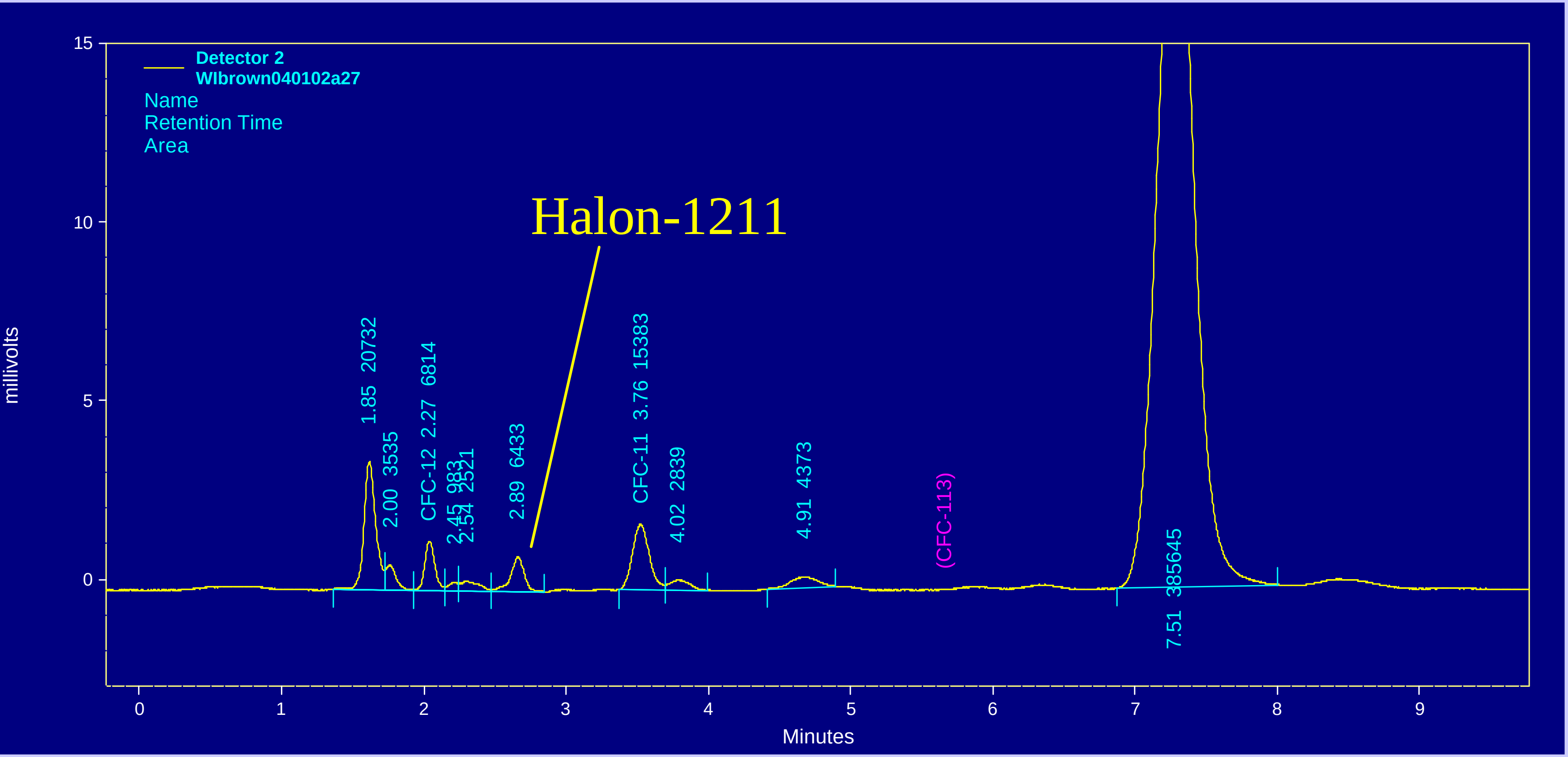
Hudson spring, Luray, VA Approximately 1970 water



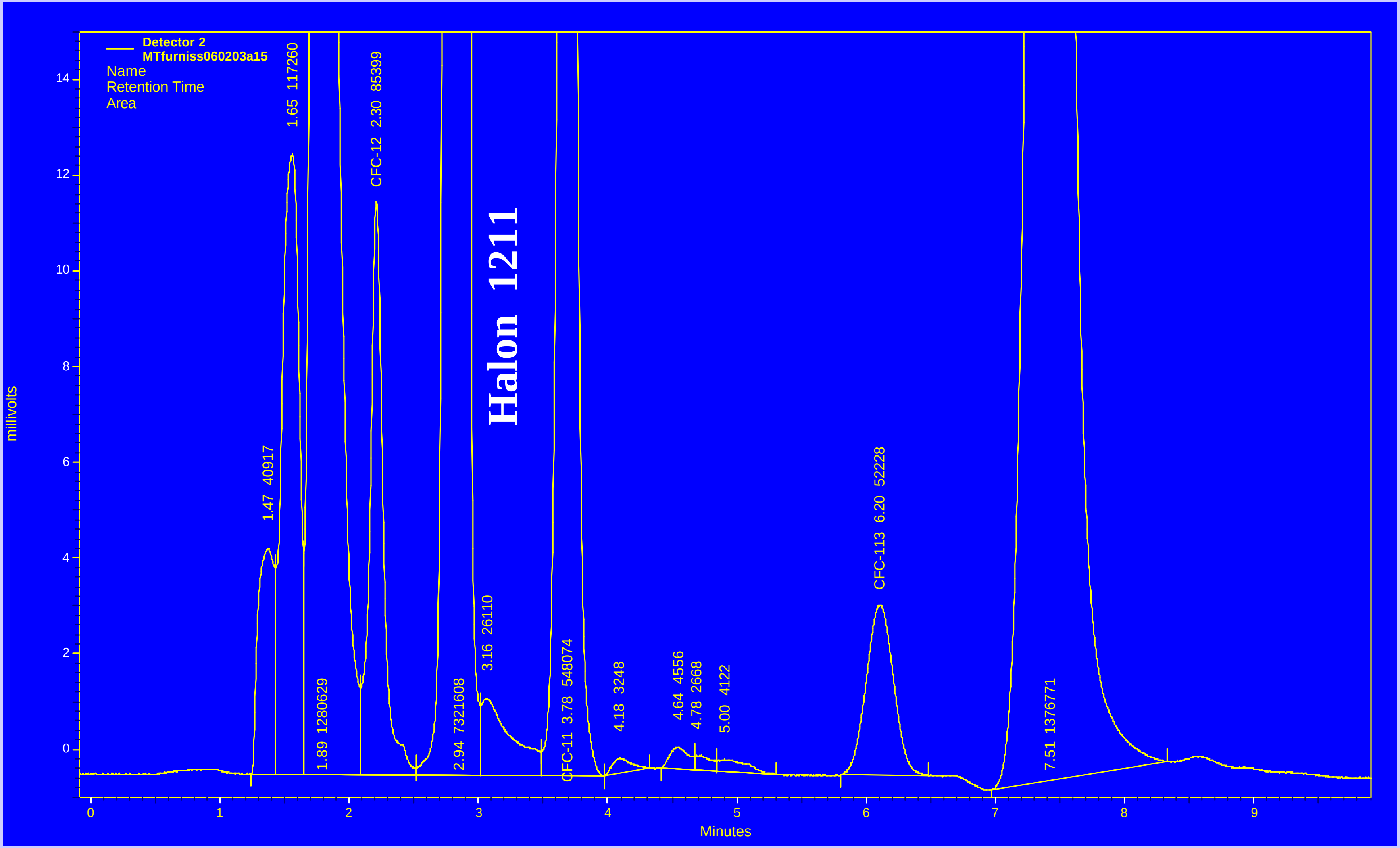
Chromatogram of 1.16 cubic centimeter of nitrogen containing a concentration of 0.59 parts per billion Halon 1211.



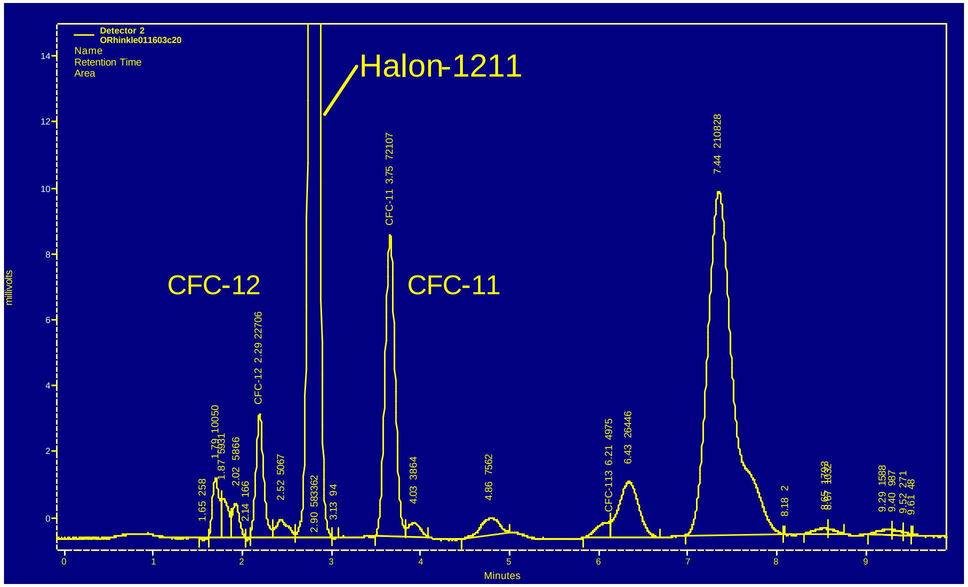
Chromatogram of Halon 1211 stripped from 30 cubic centimeters of water equilibrated with nitrogen containing 0.59 parts per billion Halon 1211 at 54^{o}F.



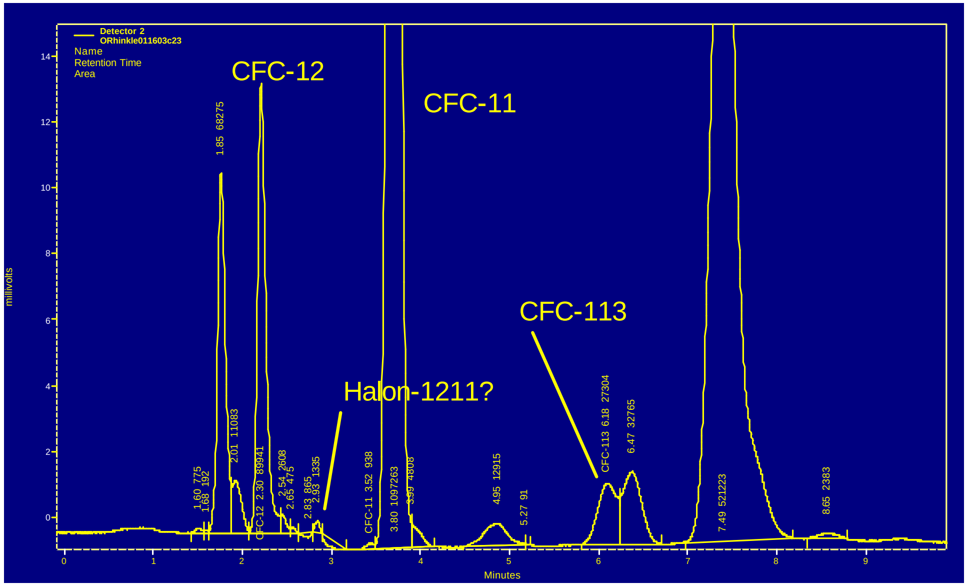
Chromatogram of water from the Round Hill well taken after 6 hours of pumping (2 months after drilling) showing a small peak for Halon 1211 between the peaks for CFC-12 and CFC-11 (2.89). This peak is not detected in ambient air and indicates the presence of ground water affected by air from the drilling process.



Ground-water sample from June 2, 2003, after loss of drilling fluid during sidewall coring process.



Well MW-N3D. Large Halon peak. CFC-11 and CFC-12 indicate mid- to late 1970s. Since CFCs came with Halon, water is older than 1970s, but cannot be dated further with CFCs because of contamination with drilling air. Possible mixture of old water and water contaminated with drilling air. Without the Halon data, we would have interpreted a CFC age that is too young.



Well MW-N4D. Trace or no Halon present. CFC data probably unaffected by drilling air. CFC data suggest a modern age for the water. Without the Halon data, we would not know that the CFCs are valid in this sample.

CONCLUSIONS

- **Use of multiple tracers and "tracer plots" can help to eliminate some mixing models and refine estimates of mean tracer age.**
- **To a first approximation, the ages and mixing fractions of many samples from karst or fractured rock can be interpreted using a simple binary mixing model. Is this the result of the sampling process?**
- **Most ground water from fractured rock or karstic aquifers is susceptible to contamination.**
- **Should include tracers in well drilling.**

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CONCLUSIONS (cont.)

- "… the concept of groundwater age has little significance" (Fontes, 1983); yet investigation of multiple environmental tracers in groundwater systems can often help to refine the interpretation of age, refine hydrologic concepts, and identify susceptibility to contamination.

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Acknowledgements

- **Chesapeake Bay Study.** Scott Phillips, Bruce Lindsey, Gary Spieran, Mike Focazio, J.K. Bohlke, Bill Burton, Colleen Donnelly.
- **Virginia Aquifer Susceptibility Study.** Dave Nelms and George Harlow.
- **Shenandoah National Park Study.** Ed Busenberg, Dave Nelms, Jerry Casile, Julian Wayland, Wandee Kirkland, Stephanie Shapiro, Brian Norton.
- **Reston Chlorofluorocarbon Laboratory.**
- **Noble Gas Laboratory of Lamont-Doherty Earth Observatory, Columbia University.**